SPECTROSCOPIC STUDIES OF LUMINESCENCE AT THE CATHODE DURING ELECTROLYSIS.

By Iturô UHARA.

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Luminescence has been observed during electrolysis in many cases, mostly at the anode, and it is attributed to the formation of a thin film of insoluble matters, for examples, oxide, hydroxide, oxygen on aluminium electrode, mercurous chloride on the surface of mercury; and the spectra are continuous. There are a few examples of luminescence at the cathode. M. Fraymann[1] observed that, when a sulphuric acid solution was electrolysed in high current density with various metals as the cathode, arc lines of the metals and H_α- and often H_β-lines were emitted by sparking through the film of hydrogen on the cathode. A. W. Dumanski and his co-workers[2]

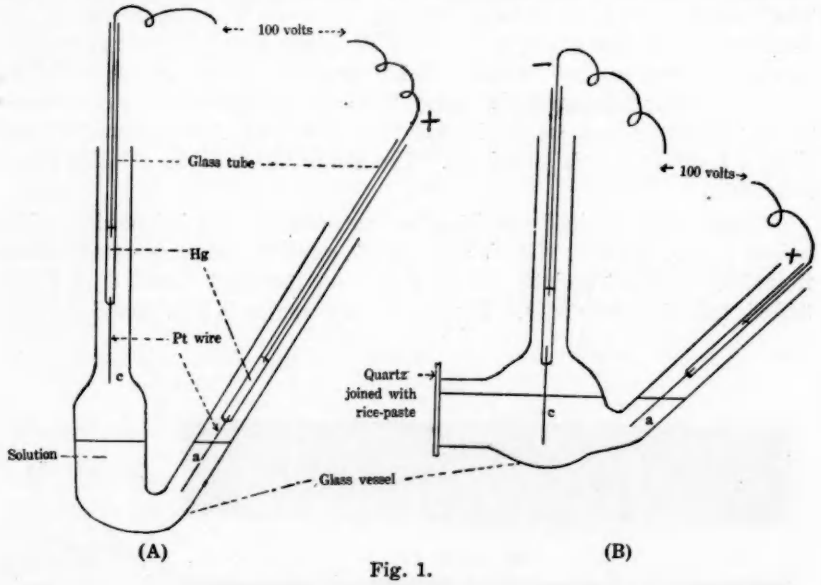

Fig. 1.

(1) M. Fraymann, *Recherches et Inventions*, **11**, 36-41; *Chem. Zentr.*, **101** (1930), I 1902.

(2) A. W. Dumanski, A. W. Banow, M. W. Lichoscherstow, *Chem. J. Ser. W. J. physik. Chem.*, **2** (1931), 806-813; *Chem. Zentr.*, **104** (1933), II, 1307.

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observed very weak luminescence when the current was reversed during electrolysis of the solutions of zinc chloride, etc., with mercury electrodes, and calcium salts and magnesium nitrate with platinum electrodes; and he remarked that this was not explicable as an oxidation reaction as in the cases of luminescence at the anode.

The writer observed luminescence at the cathode during electrolysis of the solutions of many electrolytes with electrodes of platinum wire, and studied the spectra. The apparatus for electrolysis is shown in Fig. 1(A).

The solutions of Merck's and Kahlbaum's products in the concentration of 1–3 N, or 1.5–1 N for acid solutions, were electrolysed. When the platinum electrode (c) was immersed quietly in the solution, scintillation took place over the surface of the electrode with hydrogen evolution and noise. When the voltage was too low, or when the solution was too dilute, or when the circuit was closed after the cathode (c) was immersed in the solution, only violent electrolysis was observed. This suggests that the formation of a thin film of hydrogen over the cathode under high current density is necessary. The spectra of luminescence were studied under the following conditions with Hilger's glass spectrograph of constant deviation type: current 0.2–0.5 amperes or more; current density 0.6–1.5 amperes per sq. cm. or more; slit about 0.2 mm.; photographic plates Wratten hypersensitive panchromatic plates; exposure one hour (for intense lines like D-line from sodium salt solutions a few minutes is sufficient). The temperature of the solution rose to about 80°.

The spectra obtained consist of sharp lines and are independent of the anions (NaCl, $NaNO_3$, NaOH, and Na_2CO_3 gave the same spectra). Sometimes Na^+ and Ca^{++} go into the solution from the glass vessel during electrolysis and give their lines. The spectra are shown in Fig. 2, and the wave

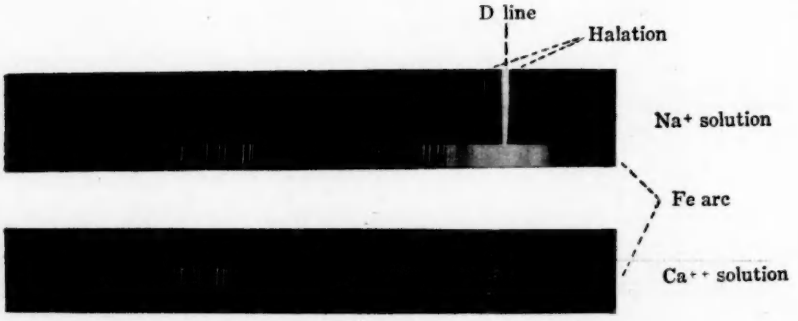

Fig. 2.

lengths (Å) of the observed lines are given in Table 1 (intensity is shown by asterisks).

Table 1.

Na^+ Solution.

Lines	Remarks
5890***, 4985, 4670, 5690**, 6164*	Due to Na I
6563* (H_α), 4860(H_β)	Due to H I
4227, 5140	Due to Ca I
3830	Due to Mg I

K^+ Solution.

4608, 4388, 4309, 4263, 4226, 4135, 4115	Spark lines of K
6563** (H_α), 4861* (H_β)	Due to H I
4849, 4654*	Due to H_2
5890**	Due to Na I
4418	Due to O(?); Kayser's table: O 4416.97; H_2 4412.25
4353	Kayser's table: Mg I 4352.1; O II 4351.38
4370	Kayser's table: O II 4369.28; O I 4368.30; Cs 4373.0
4593	Kayser's table: O II 4596.19, 4590.98; Cs 4593.2
4647	Kayser's table: O II 4649.15; Rb 4648.56
4829	Kayser's table: Cs 4830.2
4838	?

HCl Solution.

6563** (H_α), 4860 (H_β), 4340 (H_γ)	Due to H I
6032, 6327, 4491*, 4205*	Due to H_2
4520, 4548, 4165, 4120	Due to Pt; sometimes black powder of platinum is precipitated.
5896, 5688	Due to Na I
5855, 5270**, 5041, 4435	Due to Ca I
4150	Kayser's table: O II 4153.31; Al III 4150.1
6318	Due to Mg I

Table 1 (*Concluded*).

NH_4^+ Solution.

Lines	Remarks
6530* (H_α), 4860 (H_β), 4340 (H_γ)	Due to H I
5435, 4490, 5055, 4205	Due to H_2
4548	Due to Pt
6550	Due to O(?)
5270, 5350, 5140, 4455	Due to Ca

Ca^{++} Solution.

6494*, 6472**, 6470**, 6439**, 6162*, 6122*, 5858*, 5595**, 5589**, 5350, 5270**, 5189, 5042, 4878, 4586, 4455**, 4435**, 4426**, 4308*, 4303**, 4290*, 4227*	Due to Ca I
3969*, 3934*	Due to Ca II
6563(H_α)	Due to H I
5537**, 5505*, 6135*	Due to H_2
5890, 5688	Due to Na I
4390	Due to Mg II (?)
5455	Kayser's table : Sr I 5450.83 ; Hg I 5460.724

$Hg(NO_3)_2+HNO_3$ Solution.

5791, 5770, 5461**, 4358*	Due to Hg I
5890**	Due to Na I

To study the ultraviolet region an apparatus as shown in Fig. 1 (B) and Hilger's quartz spectrograph were used. Lines of metals and hydrogen were observed, but OH-band was not (this band was not observed when carbon arc was lit in hydrogen which had been passed through boiling water under one atmospheric pressure).

In electrolysis with the alternating current (100 volts) luminescence takes place sometimes on both electrodes, sometimes on one electrode of higher current density. Even with the solutions of those metallic salts (e.g. aluminium and magnesium salts) which give weak luminescence, or such luminescence as disappears in the course of time, owing to the formation of insoluble hydroxide in the electrolysis with the direct current, we can observe lumines-

cence for a long time in electrolysis with the alternating current. The spectra are the same as in the case of the direct current.

Solutions of Ba^{++}, Sr^{++}, Mg^{++}, Al^{+++}, Cd^{++}, Zn^{++}, Hg_2^{++}, Fe^{++}, Co^{++}, Mn^{++}, Bi^{+++}, and Sn^{++} gave those lines which are observed in their arc spectra.

Summary.

If the current density at the cathode is high enough for the formation of a thin film of hydrogen in the electrolysis of the electrolyte solutions with platinum wire electrodes, considerably intense cathode luminescence takes place; and the spectra are in most cases the same as the arc spetra (sometimes spark spectra) of the elements forming cations, and further Balmer lines of H and the molecular spectra of H_2 are often observed.

In conclusion the author wishes to express his best thanks to Mr. H. Wakesima for his kind advice and assistance and to Mr. A. Tamai and Mr. M. Nakamura for their assistance.

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TETRADECENOIC AND DODECENOIC ACIDS IN SPERM OIL. I. TETRADECENOIC AND DODECENOIC ACIDS IN SPERM BLUBBER OIL.*

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Sperm oil is obtained from the sperm whale, *Physeter macrocephalus* L., and the oil obtained from the body blubber is generally kept separate from that of the head cavities. Sperm blubber (or body) oil and sperm head oil are, therefore, known in the foreign market. In this country, however, four kinds of oils are differentiated, i.e. head oil, blubber oil (skin oil), intestine oil and bone oil; the blubber oil is obtained exclusively from the blubber under the skin and has the largest yield, while the intestine oil is obtained from the intestines and the surrounding flesh. Sperm oil is frequently allowed to crys-

* Translated from the Japanese text published in *J. Chem. Soc. Japan*, **56** (1935), 1050.

tallise at a low temperature and subjected to pressure, by which the solid portion is removed and the oil having a low cold-test is obtained. The solid portion is used for further preparation of spermaceti. However, these separative operations are not generally carried out in this country. The constituents of sperm oil have been studied since a very earlier date. Far back in about 1820, Chevreul in his classic studies found cetyl alcohol in spermaceti, and also pointed out the presence of some peculiar constituents in sperm head oil. Afterwards there have appeared many studies, among which those of Hofstädter,[1] Bull,[2] Fendler,[3] Walker and Warburton,[4] Procter and Bennet,[5] Dunlop,[6] Lewkowitsch,[7] Allen,[8] and Nakajima[9] may be mentioned. Much contributions have been made recently to the knowledge of the constituents of sperm oil by the closer studies of Tsujimoto[10] on the fatty acids and the alcohols of sperm head oil, André and François[11] on the alcohols of sperm head oil and spermaceti, and Hilditch and Lovern[12] on the fatty acids, the alcohols as well as the component esters of sperm blubber and head oils. One of the present authors (Toyama)[13] also examined the fatty acids and the alcohols of sperm blubber oil. For a thorough account of the results set forth by these authors the original papers should be consulted. Only a short review on the literature relating to the theme of the present paper, i.e. tetradecenoic acid $C_{14}H_{26}O_2$ and dodecenoic acid $C_{12}H_{22}O_2$ in sperm oil, is given below. Tsujimoto[14] isolated a tetradecenoic acid from sperm head oil and established its constitution as $\Delta^{5:6}$-tetradecenoic acid. He inferred the presence of a tetradecenoic acid also in sperm blubber oil. The same author[15] found a tetradecenoic acid also in Tsuzu oil (seed oil of *Tetradenia glauca* Matsum.), the constitution of which was, however, proved to be $\Delta^{4:5}$-tetradecenoic acid. He assigned the name physeteric acid to $\Delta^{5:6}$-acid in sperm head oil and the name tsuzuic acid to $\Delta^{4:5}$-acid in Tsuzu oil. According to Hilditch and Lovern,[16] on the other hand, the fatty acids of sperm head oil contain 14% of tetradecenoic acid and 4% of dodecenoic acid, whilst the fatty acids of sperm blubber oil contain 4% of tetradecenoic acid, but no dodecenoic acid.

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(1). (2), (3). (4), (5), (6), (7) Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes", Vol. II (6th Edition), 875-876.

(8) "Commercial Organic Analysis", Vol. II (3rd Edition), Part I, 204-205.

(9) Dissertation, College of Engineering, Tokyo Imperial University (1917).

(10) *J. Soc. Chem. Ind., Japan*, **24** (1921), 41; **26** (1923), 608; **29** (1926), 102.

(11) *Compt. rend.*, **183** (1926), 663; **185** (1927), 279.

(12) *J. Soc. Chem. Ind.*, **47** (1928), 105 T; **48** (1929), 359 T; **48** (1929), 365 T.

(13) *J. Soc. Chem. Ind., Japan*, **30** (1927), 519, 527.

(14) *Loc. cit.*, (10).

(15) *J. Soc. Chem. Ind., Japan*, **29** (1926), 105; *Reports of the Tokyo Imperial Industrial Research Laboratory*, **23** (1928), No. 3.

(16) *Loc. cit.*, (12).

As for the constitutions of these acids, they stated that tetradecenoic acid in head oil is identical with physeteric acid ($\Delta^{5:6}$-acid) discovered by Tsujimoto, whereas tetradecenoic acid in blubber oil is $\Delta^{9:10}$-acid which is identical with the acid found in South Georgia whale oil by Armstrong and Hilditch.[17] The constitution of dodecenoic acid in head oil was stated to be $\Delta^{3:4}$-acid. However, Hilditch and Lovern did not separate the individual acids. In their experiments the mixed fatty acids were treated by the lead-soap-alcohol method, the methyl esters of the liquid fatty acids were fractionated, and the fractions corresponding to C_{14}- and C_{12}-acids respectively were separately collected. The constitutions of tetradecenoic and dodecenoic acids were derived from the results of the permanganate oxidation of these fractions which, however, were still contaminated with a large proportion of the methyl esters of saturated acids. In this connection it may be noted here that a dodecenoic acid, named linderic acid, was first isolated by Iwamoto[18] from the seed oil of *Lindera obtusiloba*, and its constitution was established by him as $\Delta^{4:5}$-acid.[19] Toyama[20] in his previous work on the sperm blubber oil, obtained some indications of the presence, though in a small proportion, of tetradecenoic acid, but the separation of this acid could not be attained. In a continuation of the previous work, we have undertaken the present experiments with a view to separate tetradecenoic acid starting with a large quantity of sperm blubber oil, and to ascertain by a closer examination of its constitution whether it differs from physeteric acid, as stated by Hilditch and Lovern, or not. Furthermore we have separated a dodecenoic acid from sperm blubber oil as well as from head oil, and examined its constitution. In this paper the experimental results concerning tetradecenoic and dodecenoic acids in blubber oil are described, while those of dodecenoic acid in head oil will be given in a succeeding paper.

In dealing with the unsaponifiable matter of sperm blubber oil, as described in a separate communication, a fatty acid fraction was obtained, mainly from the barium soaps soluble in acetone, in the course of the operations carried out for the separation of unsaponifiable matter. It contained large proportions of highly unsaturated acids and lower members of monoethylenic acids. The greater part of tetradecenoic and dodecenoic acids originally present in sperm blubber oil was thought to have entered into this fraction. For the present experiments this fraction was used as the starting

(17) *J. Soc. Chem. Ind.*, **44** (1925), 180 T.

(18) *J. Soc. Chem. Ind., Japan*, **24** (1921), 1143; **26** (1923), 708.

(19) It is also reported that Grün and his co-workers found dodecenoic ($\Delta^{11:12}$?) and tetradecenoic ($\Delta^{13:14}$?) acids together with $\Delta^{9:10}$-decenoic acid in butter fat. Cp. *Z. angew. Chem.*, **37** (1924), 228.

(20) *Loc. cit.*, (13).

material. It was first converted into the methyl esters, and the latter fractionated, by which the fraction boiling below 170°/15 mm. was separately collected. This was saponified, the free fatty acids obtained was further fractionally distilled, and two fractions, (a) 192–197°/15 mm. and (b) 172–177°/15 mm., were separated. The fraction (a) was treated with lead acetate in 90% alcoholic solution under strong cooling, the precipitate of the lead soaps of saturated acids were filtered off, and the filtrate yielded tetradecenoic acid. The same treatment of the fraction (b) yielded dodecenoic acid. Tetradecenoic acid thus obtained was then converted into dihydroxymyristic acid by Hazura's method, and its methyl ester was subjected to the permanganate oxidation in acetone. After saponification of the ester contained in the oxidation products, *n*-nonoic acid $CH_3\cdot(CH_2)_7\cdot COOH$ and glutaric acid $HOOC\cdot(CH_2)_3\cdot COOH$ were identified, and consequently the constitution of dihydroxymyristic acid was shown to be $CH_3\cdot(CH_2)_7\cdot CHOH\cdot CHOH\cdot(CH_2)_3\cdot COOH$. Hence, the constitution of tetradecenoic acid is $\Delta^{5:6}$-tetradecenoic acid which is expressed by the formula $CH_3\cdot(CH_2)_7\cdot CH{=}CH\cdot(CH_2)_3\cdot COOH$. Tetradecenoic acid in sperm blubber oil was thus proved to be identical with physeteric acid in sperm head oil; no evidence was obtained to indicate the presence of $\Delta^{9:10}$-tetradecenoic acid which was stated by Hilditch and Lovern to occur in sperm blubber oil. Methyl dihydroxylaurate prepared from dodecenoic acid was subjected to oxidation in the same manner as methyl dihydroxymyristate, and *n*-heptoic acid $CH_3\cdot(CH_2)_5\cdot COOH$ and glutaric acid $HOOC\cdot(CH_2)_3\cdot COOH$ were identified after saponification of the ester in the oxidation products. From these results dihydroxylauric acid was found to have the formula $CH_3\cdot(CH_2)_5\cdot CHOH\cdot CHOH\cdot(CH_2)_3\cdot COOH$, and consequently the constitution of dodecenoic acid was shown to be $\Delta^{5:6}$-dodecenoic acid which is expressed by the formula $CH_3\cdot(CH_2)_5CH{=}CH\cdot(CH_2)_3\cdot COOH$. $\Delta^{3:4}$-Dodecenoic acid, which was stated by Hilditch and Lovern to occur in sperm head oil, could not be detected. We propose to assign to $\Delta^{5:6}$-decenoic acid the name denticetic acid[21] in order to distinguish it from its isomer linderic acid ($\Delta^{4:5}$-dodecenoic acid).

Experimental.

1. Separation of Tetradecenoic Acid. As described in a succeeding paper[22] dealing with the unsaponifiable constituents of sperm blubber oil, a specimen of sperm blubber oil having d_4^{25} 0.8735, n_D^{25} 1.4635, acid value 0.85, saponification value 126.8, iodine value (Wijs) 82.6 and unsaponifiable matter 38.98% was heated with a little excess of barium hydroxide and water in an autoclave under 5–6 atm. for one hour, and the reaction products

(21) Derived from *Denticete*.

(22) This Bulletin, **10** (1935), 579.

consisting of barium soaps and free unsaponifiable matter were extracted with acetone. The substances obtained on distilling off the solvent from the acetone solution were, however, contaminated with a small proportion of barium soaps and neutral oil which escaped saponification. They were heated with an excess of alcoholic potash to effect a complete saponification of the remaining neutral oil, the soaps were decomposed with hydrochloric acid, and the unsaponifiable matter contaminated with a small amount of free fatty acids was taken up with ether. The ethereal solution was then washed with potassium hydroxide solution which dissolved out free fatty acids as their potassium soaps. For the present experiments the fatty acids regenerated from the potassium soaps thus obtained were used as the starting material. They were obtained in a yield of 2.4% of the oil, and showed neutralisation value 199.1 and iodine value 133.0. Five hundred grams of these fatty acids, corresponding to 21 kg. of the oil, were refluxed with an equal amount of methanol containing 2.5% of hydrogen chloride for 30 minutes, and the resulting methyl esters were separated from excess of methanol and some unchanged fatty acids. These were distilled, and there was obtained 26 g. of a fraction boiling below 170°/15 mm. and having saponif. value 234.8 and iodine value 78.3. This fraction was converted into free fatty acids, and the latter were fractionated. Two fractions were separately collected; (a) b. p. 192–197°/15 mm., 8.4 g. and (b) b. p. 172–177°/15 mm., 1.9 g. The fraction (a) showed neutr. value 249.8 and iodine value 84.9, and was used for further separation of tetradecenoic acid, whilst the fraction (b) was used for the separation of dodecenoic acid.

The fraction (a) was dissolved in 90% alcohol, and a solution of lead acetate (about half the theoretical quantity) in 90% alcohol was added, the total quantity of 90% alcohol being about 10 times the quantity of the fraction (a). The solution was cooled down to −15°, the precipitate of lead soaps were filtered off, and the filtrate yielded tetradecenoic acid $C_{14}H_{26}O_2$ having the following constants (Found: C, 74.39; H, 11.49. Calc. for $C_{14}H_{26}O_2$: C, 74.27; H, 11.58%).

d_4^{15} 0.9081, d_4^{20} 0.9046, n_D^{15} 1.4571, n_D^{20} 1.4552, mol. refraction (based on the data at 15°) 67.86 (calc. for $C_{14}H_{26}O_2$ Γ_1: 67.92), neutr. value 248.8 (calc. 248.0), iodine value 107.8 (calc. 112.2).

The hydrogenation product of tetradecenoic acid gave myristic acid $C_{14}H_{28}O_2$ which showed neutr. value 244.9 (calc. 245.8), m.p. and mixed m.p. 53.5–54° after recrystallisation from 80% alcohol. On oxidising tetradecenoic acid by Hazura's method, it yielded dihydroxymyristic acid $C_{14}H_{28}O_4$ which showed neutr. value 215.0 (calc. 215.6) and m.p. 118.5–119° after recrystallisation from 75% alcohol.

2. **Oxidation of Methyl Dihydroxymyristate.** Dihydroxymyristic acid described above was converted into its methyl ester by using hydrogen chloride in methanol. The methyl ester (3.5 g.) thus obtained was dissolved in 35 c.c. of acetone, and 7 g. of powdered potassium permanganate was added in small portions. The liquid was refluxed on the water-bath for one hour, and then acetone was removed by distillation. The residue was mixed with 70 c.c. of water, and a current of sulphur dioxide was passed into the mixture until the excess of potassium permanganate and the insoluble oxides of manganese disappeared completely. The oxidation products were extracted by using 400 c.c. of ether, and after the ethereal solution was concentrated to less than half its original volume, it was then shaken with potassium carbonate solution by which the acidic substances were dissolved out as their potassium salts, while the neutral substances were left in ethereal solution. The aqueous solution containing the potassium salts was separated, and after addition of 2 g. of potassium hydroxide, the solution was heated on

the water-bath so as to saponify the acid ester contained in the oxidation products. After acidification with hydrochloric acid, the acidic substances liberated were taken up with ether. The ethereal solution was washed with water, and on removal of ether by distillation, there remained 2.3 g. of acidic substances. The low yield is thought to be due either to an incomplete oxidation with potassium permanganate or to the loss caused by washing the ethereal solution with water. The acidic substances were treated with 60 c.c. of petroleum ether (b.p. below 60°) to effect a separation into petroleum ether solution and insoluble portion. On removal of the solvent from the petroleum ether solution by heating on the water-bath, the residue was then distilled by heating in the oil-bath and there was obtained about 1 g. of colourless distillate boiling below 193°/100 mm. and having neutr. value 353.1 (calc. for $C_9H_{18}O_2$: 354.8) and n_D^{20} 1.4318. The amide prepared from the distillate was found to be *n*-nonoic acid amide which showed m.p. and mixed m.p. 98.5–99°[23] when recrystallised from 50% alcohol (Found: N, 9.00. Calc. for $C_9H_{19}ON$: N, 8.91%).

The portion insoluble in petroleum ether (0.8 g.) consisted of a crystalline solid. It crystallised from benzene in lustrous needles which showed neutr. value 845.8 (calc. for $C_5H_8O_4$: 849.7) and m.p. 97–97.5° (Found: C, 45.49; H, 6.21. Calc. for $C_5H_8O_4$: C, 45.43; H, 6.11%). The melting point was not lowered when the substance was admixed with a pure specimen of glutaric acid, m.p. 97.5–98°.

3. **Separation of Dodecenoic Acid.** The fraction (b) described above had neutr. value 282.4 and iodine value 83.5. It was dissolved in 90% alcohol, and a solution of lead acetate (approximately theoretical quantity) in 90% alcohol was added, the total quantity of 90% alcohol used being about 10 times the quantity of the fraction (b). The solution was cooled down to −15°, the precipitated lead soaps were filtered, and there was obtained dodecenoic acid $C_{12}H_{22}O_2$ having the following constants from the filtrate (Found: C, 72.99; H, 11.30. Calc. for $C_{12}H_{22}O_2$: C, 72.67; H, 11.19%).

d_4^{15} 0.9130, n_D^{15} 1.4535, mol. refraction 58.72 (calc. for $C_{12}H_{22}O_2$ $\bar{F}_1$: 58.69), neutr. value 232.0 (calc. 283.1), iodine value 118.7 (calc. 128.1).

Oxidation of dodecenoic acid by Hazura's method gave dihydroxylauric acid $C_{12}H_{24}O_4$ which had neutr. value 240.9 (calc. 241.6) and m.p. 106–107° after recrystallisation from ether. Since the precipitate of lead soaps obtained in the final separative operation for dodecenoic acid was thought to contain a considerable amount of lead dodecenoate besides the lead soaps of saturated acids, the fatty acids liberated from the precipitate on acidification were subjected to Hazura's oxidation method so as to separate dihydroxylauric acid which showed neutr. value 241.0 (calc. 241.6) and m.p. 105–106° after recrystallisation from ether.

4. **Oxidation of Methyl Dihydroxylaurate.** The specimens of dihydroxylauric acid were combined, and converted into the methyl ester by using hydrogen chloride in methanol. The methyl ester (1.1 g.) was dissolved in 10 c.c. of acetone, and 2 g. of powdered potassium permanganate was added in small portions. After the liquid had been heated on the water-bath under a reflux condenser for one hour, acetone was removed by distillation, 20 c.c. of water was added to the residue, and a current of sulphur dioxide was passed into the solution, until the excess of permanganate and the insoluble oxides of manganese disappeared completely. The solution was shaken with ether in order to extract the oxidation products. The ethereal solution was treated with potassium carbo-

(23) The specimen of *n*-nonoic acid amide used for the mixed melting point test was prepared from *n*-nonoic acid which was obtained by the ozonolysis of oleic acid.

nate solution, and the acidic substances were dissolved out as their potassium salts. The aqueous solution containing potassium salts were separated from the ethereal solution, a little potassium hydroxide was added, and the solution was heated on the water-bath to effect the saponification of the acid ester contained in the oxidation products. The free acidic substances obtained on acidification with hydrochloric acid were once taken up with ether, the ethereal solution was washed with water, and after removal of ether by distillation the residue was treated with petroleum ether, yielding the petroleum ether solution and the insoluble portion.

The petroleum ether solution was heated on the water-bath to distill off the solvent, and there was obtained a residue (0.5 g.) which, after being washed with a little water, showed neutr. value 439.8 (calc. for $C_7H_{14}O_2$: 431.5) and n_D^{20} 1.4235, and appeared to be *n*-heptoic acid. The amide prepared from it melted at 91–92° after recrystallisation from petroleum ether, and no depression of melting point was observed when the amide was admixed with various proportions of a pure specimen of *n*-heptoic acid, m.p. 94.5–95°.(24)

The portion insoluble in petroleum ether (0.2 g.) was recrystallised from benzene in needles which had neutr. value 846.2 (calc. for $C_5H_8O_4$: 849.7) and melted at 95–96°. The melting point was not lowered when the substance was admixed with various proportions of a pure specimen of glutaric acid $C_5H_8O_4$, m.p. 97.5–98°.

Summary.

Tetradecenoic acid $C_{14}H_{26}O_2$ and dodecenoic acid $C_{12}H_{22}O_2$ have been separated from sperm blubber oil. They are converted into dihydroxymyristic acid $C_{14}H_{28}O_4$ and dihydroxylauric acid $C_{12}H_{24}O_4$ respectively, and the methyl esters of these hydroxy-derivatives are subjected to the permanganate oxidation in acetone. From the results of an examination of the oxidation products, the following constitutions have been established:

Tetradecenoic acid	$CH_3{\cdot}(CH_2)_7{\cdot}CH{=}CH{\cdot}(CH_2)_3{\cdot}COOH$,
Dodecenoic acid	$CH_3{\cdot}(CH_2)_5{\cdot}CH{=}CH{\cdot}(CH_2)_3{\cdot}COOH$.

It is thus seen that tetradecenoic acid in sperm blubber oil is identical with physeteric acid ($\Delta^{5:6}$-tetradecenoic acid) in sperm head oil, whilst dodecenoic acid in sperm blubber oil, to which the name denticetic acid is assigned, is $\Delta^{5:6}$-acid and is an isomer of linderic acid ($\Delta^{4:5}$-dodecenoic acid) in the seed oil of *Lindera obtusiloba*.

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(24) For the preparation of *n*-heptoic acid amide used for the mixed melting point test, castor oil was subjected to dry distillation, and a fraction consisting of *n*-heptyl aldehyde (b.p. 153–154°) was separated. This was oxidised with potassium bichromate and sulphuric acid, the product was fractionated, and a fraction of *n*-heptoic acid (b.p. 220–224°) was separated and then converted into its amide.

TETRADECENOIC AND DODECENOIC ACIDS IN SPERM OIL. II. DODECENOIC ACID IN SPERM HEAD OIL.*

By Yoshiyuki TOYAMA and Tomotaro TSUCHIYA.

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As described in the preceding paper,[1] tetradecenoic and dodecenoic acids were separated from sperm blubber oil, and their constitutions were determined with the results that tetradecenoic acid was proved to be identical with physeteric acid ($\Delta^{5:6}$-tetradecenoic acid) found by Tsujimoto in sperm head oil, whilst dodecenoic acid, named denticetic acid, was found to be $\Delta^{5:6}$-dodecenoic acid and not $\Delta^{3:4}$-dodecenoic acid which was stated by Hilditch and Lovern[2] to occur in sperm head oil. We have now separated dodecenoic acid from sperm head oil, and examined whether its constitution is really $\Delta^{3:4}$-dodecenoic acid as stated by Hilditch and Lovern or not.

In these experiments, the head oil was first subjected to methanolysis, and the product consisting of the methyl esters and the free unsaponifiable matter (chiefly higher alcohols) was fractionated. The fraction boiling below 150°/15 mm. was separately collected, the unsaponifiable matter was removed from it, and the fatty acids were separated. These were treated with lead acetate in 90% alcoholic solution at the room temperature. However, the lead soaps of saturated acids were not precipitated to a sufficient extent; the liquid acids obtained from the filtrate appeared from their iodine value (41.6) to contain still more than 50% of saturated acids. The liquid acids were then fractionated, and a fraction corresponding to C_{12}-acids was separated. It was then subjected to the bromo-ester method of Grün and Janko;[3] i.e. it was converted into the methyl esters and then brominated, the product was distilled so as to remove the saturated methyl esters, leaving the bromides of unsaturated methyl esters as the residue which was debrominated afterward to regenerate unsaturated methyl esters. These were saponified to obtain free fatty acids which had iodine value 98.2 and contained still saturated acids in not insignificant amount. In order to remove the saturated acids as far as possible, the fatty acids obtained above were treated with lead acetate in 90% alcohol, the solution was cooled down to -15°, and the precipitate of

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* Translated from the Japanese text published in *J. Chem. Soc. Japan*, **56** (1935), 1055.

(1) This Bulletin, **10** (1935), 563.

(2) *J. Soc. Chem. Ind.*, **47** (1928), 105T.

(3) *Z. deuts. Oel- u. Fett-Ind.*, **41** (1921), 553, 572.

lead soaps was filtered off. The liquid acids obtained from the filtrate consisted essentially of dodecenoic acid. For the determination of the position of ethylenic linking in dodecenoic acid, it was first converted into dihydroxylauric acid by Hazura's method, and the methyl ester of this hydroxy-derivative was oxidised with potassium permanganate in acetone. Among the oxidation products, after saponification of the acid ester, *n*-heptoic acid and glutaric acid were identified. Accordingly the constitution of dihydroxylauric acid was found to be expressed by the formula $CH_3\cdot(CH_2)_5\cdot CHOH\cdot CHOH\cdot(CH_2)_3\cdot COOH$, and consequently the constitution of dodecenoic acid is $\Delta^{5:6}$-dodecenoic acid which is expressed by the formula $CH_3\cdot(CH_2)_5\cdot CH{=}CH\cdot(CH_2)_3\cdot COOH$. It is seen from these results that dodecenoic acid in sperm head oil is nothing else than denticetic acid ($\Delta^{5:6}$-dodecenoic acid) found in sperm blubber oil. $\Delta^{3:4}$-Dodecenoic acid described by Hilditch and Lovern is not found.

Experimental.

1. **Separation of Dodecenoic Acid.** Sperm head oil used for the present experiments deposited a considerable amount of crystalline solid at the room temperature, and had the following characteristics: d_4^{40} 0.8654, n_D^{40} 1.4523, acid value 3.1, saponification value 147.7, iodine value (Wijs) 53.4, unsaponifiable matter 36.52%. It was first pressed at the room temperature, the solid portion was removed, and the clear oil was obtained with about 80% yield. An equal amount of methanol containing 3% of sodium hydroxide was added to the clear oil, and the mixture was well shaken for 40 minutes at about 40°, when it became homogeneous due to the formation of methyl esters and free unsaponifiable matter. A large quantity of water was then added to the solution, and the oily layer separated was washed with water to remove the contaminated soaps which had been formed to a slight extent in the course of methanolysis. The product of methanolysis thus obtained consisted of the methyl esters and the free unsaponifiable matter (mainly higher alcohols). It was distilled, and the fraction boiling below 150°/15 mm. was separated, the yield of this fraction being 139 g. from 4 kg. of the product of methanolysis. This fraction was saponified, and the unsaponifiable matter was removed by extraction with ether in the usual way. The fatty acids liberated from the soap solution was dissolved in 90% alcohol, lead acetate (approximately the theoretical quantity) dissolved in 90% alcohol was added, and the solution was kept at the room temperature over a night. The precipitated lead soaps were filtered, and the fatty acids were regenerated from the filtrate; yield 91 g., neutr. value 298.9 and iodine value 41.6. These were distilled, and a fraction boiling at 170–180°/15 mm. and having neutr. value 285.8 and iodine value 50.2 was separately collected in a yield of 31 g. It was converted into the methyl esters, and the latter were brominated in ethereal solution. The product of bromination was then distilled until the rate of distillation became very slow at about 110°/5 mm., when the distillation was discontinued. The residue was treated with zinc powder and sulphuric acid in methanol,(4) the debrominated methyl esters were converted into the free fatty acids which were then distilled, yielding 8.5 g. of a fraction

(4) Kimura, *J. Soc. Chem. Ind., Japan*, **34** (1931), 958.

having b.p. 172–177°/15 mm., neutr. value 283.1 and iodine value 98.2. This fraction was then dissolved in 90% alcohol, and lead acetate (approximately the theoretical quantity) dissolved in 90% alcohol was added, the total quantity of 90% alcohol being about 10 times the quantity of the fatty acid fraction. The solution was cooled down to −15°, the precipitate of lead soaps was removed by filtration, and there was obtained from the filtrate 4.5 g. of fatty acids which were found to consist mainly of dodecenoic acid (Found: C, 72.71; H, 11.22. Calc. for $C_{12}H_{22}O_2$: C, 72.67; H, 11.19%).

d_4^{15} 0.9132, d_4^{20} 0.9097, n_D^{15} 1.4538, n_D^{20} 1.4519, mol. refraction (based on the data at 15°) 58.74 (calc. for $C_{12}H_{22}O_2$ ⌐1: 58.69), neutr. value 283.0 (calc. 283.1), iodine value 122.5 (calc. 128.1).

Hydrogenation of dodecenoic acid yielded lauric acid $C_{12}H_{24}O_2$, which after recrystallisation from 80% alcohol, showed neutr. value 280.4 (calc. 280.3), m.p. and mixed m.p. 43.5–44°. On oxidising dodecenoic acid by Hazura's method there was obtained dihydroxylauric acid $C_{12}H_{24}O_4$ which showed neutr. value 241.0 (calc. 241.6) and m.p. 106–107° when recrystallised from ether (Found: C, 61.93; H, 10.51. Calc. for $C_{12}H_{24}O_4$: C, 62.02; H, 10.42%). The melting point was unaltered when it was admixed with dihydroxylauric acid prepared from dodecenoic acid which was isolated from sperm blubber oil, but it melted at about 90° when admixed with dihydroxylauric acid[6] prepared from linderic acid.[5]

The precipitate of lead soaps, which was removed by the final separative operation for dodecenoic acid, contained a considerable proportion of lead dodecenoate besides the lead soaps of saturated acids, and the fatty acids regenerated from the precipitate of lead soaps yielded a crystalline product by Hazura's method, from which dihydroxylauric acid having neutr. value 241.1 and m.p. 106–107° was easily obtained by a single recrystallisation from ether.

2. **Oxidation of Methyl Dihydroxylaurate.** Dihydroxylauric acid obtained above was converted into its methyl ester by means of hydrogen chloride in methanol. The methyl ester (3.2 g.) was dissolved in 30 c.c. of acetone, and 6 g. of potassium permanganate was added in small portions. The mixture was gently boiled on the water-bath under a reflux condenser for one hour, and then acetone was removed by distillation. The residue was mixed with 60 c.c. of water, and a current of sulphur dioxide was passed into the mixture, until the excess of permanganate and the insoluble oxides of manganese disappeared completely. The oxidation products were extracted by shaking the solution with 300 c.c. of ether, and the ethereal solution was separated and washed with potassium carbonate solution, by which the acidic substances were dissolved out as their potassium salts. On distilling off ether from the ethereal solution there remained 0.2 g. of neutral substances which escaped oxidation. The aqueous solution containing potassium salts was heated on the water-bath with the addition of potassium hydroxide to

(5) The methyl esters of the mixed fatty acids prepared from the seed oil of *Lindera obtusiloba* were fractionated, a fraction boiling at 136–142°/15 mm. was separately collected, and the fatty acids liberated from this fraction were oxidised by Hazura's method. The product was recrystallised from ether, yielding dihydroxylauric acid melting at 100–101° (Iwamoto gave m.p. 102°). Its methyl ester was subjected to permanganate oxidation in acetone. Caprylic acid and methyl hydrogen succinate were identified among the oxidation products, and consequently the constitution of linderic acid was confirmed to be $\Delta^{4:5}$-dodecenoic acid which had been established by Iwamoto.

(6) Iwamoto, *J. Soc. Chem. Ind., Japan*, **24** (1921), 1143; **26** (1923), 708.

saponify the acid ester. After acidification with hydrochloric acid, sodium chloride was added to the solution, and the liberated acidic substances were extracted with 300 c.c. of ether. The ethereal solution was washed with water containing sodium chloride, and on removal of ether by distillation there was obtained 2.9 g. of acidic substances. These were further treated with 50 c.c. of petroleum ether, and the insoluble portion was separated from the petroleum ether solution. On removal of the solvent from the petroleum ether solution by heating on the water-bath, the residue was then subjected to distillation by which about 1 g. of colourless distillate boiling below 170°/100 mm. was separately collected. It had neutr. value 437.5 (calc. for heptoic acid $C_7H_{14}O_2$: 431.2) and n_D^{20} 1.4222, and the amide prepared from it crystallised from petroleum ether in lustrous laminae; it melted at 94.5–95° both alone or admixed with a pure specimen of *n* heptoic acid amide (Found: N, 10.83. Calc. for $C_7H_{15}ON$: N, 10.85%).

The portion insoluble in petroleum ether (0.4 g.) consisted of a white crystalline solid. Recrystallisation from benzene yielded needle-shaped crystals of glutaric acid $C_5H_8O_4$; neutr. value 851.2 (calc. 849.7), m.p. and mixed m.p. 97.5–98° (Found: C, 45.40; H, 6.05. Calc. for $C_5H_8O_4$: C, 45.43; H, 6.10%).

Summary.

Dodecenoic acid $C_{12}H_{22}O_2$ has been isolated from sperm head oil, and methyl dihydroxylaurate $C_{13}H_{26}O_4$ prepared from it has been subjected to permanganate oxidation in acetone. On examining the oxidation products the constitution of dodecenoic acid has been proved to be $CH_3{\cdot}(CH_2)_5{\cdot}CH{=}CH{\cdot}(CH_2)_3{\cdot}COOH$. It is thus seen that dodecenoic acid in sperm head oil is identical with denticetic acid ($\Delta^{5:6}$-dodecenoic acid) in sperm blubber oil described in the preceding paper.

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HEXADECENOL AND TETRADECENOL IN SPERM HEAD OIL.*

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The higher alcohols contained in the unsaponifiable matter of sperm oil have hitherto been studied by many authors, among whom Tsujimoto,[1]

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(1) *J. Soc. Chem. Ind., Japan*, **24** (1921), 41.

André and François,[2] and Hilditch and Lovern[3] deserve a special mention. For a thorough description of the results set forth by these authors the original papers should be consulted; only a short review on the literature relating to the theme of the present paper, i.e. hexadecenol $C_{16}H_{32}O$ and tetradecenol $C_{14}H_{28}O$ in sperm oil, is given below. Tsujimoto stated the possible existence of hexadecenol in sperm head oil, but he found no tetradecenol. André and François, in their studies on the unsaturated alcohols of sperm head oil, found neither hexadecenol nor tetradecenol. Hilditch and Lovern found 4% of hexadecenol in the unsaponifiable matter of sperm head oil, but no hexadecenol in sperm blubber oil. One of us (Toyama)[4] concluded in his previous study that hexadecenol could have been present, if any, only in a very minute amount in sperm blubber oil. The foregoing notes show that though the presence of hexadecenol in sperm oil has been pointed out by a few authors, it has not been isolated with certainty, and nothing is known of its constitution. Tetradecenol has so far never been found in sperm oil and other fatty oils.

In the experiments of the separation of denticetic acid ($\Delta^{5:6}$-dodecenoic acid) from sperm head oil, as described in the preceding paper,[5] the product of methanolysis consisting of the methyl esters and the free unsaponifiable matter was first fractionated. The fatty acids and the unsaponifiable matter were separated from the lowest fraction boiling below 150°/15 mm. Whilst the fatty acids were worked up further for the separation of dodecenoic acid, a comparatively high iodine value of the unsaponifiable matter pointed to the possible presence of some lower members of unsaturated alcohols, besides oleyl alcohol, in sperm head oil. Accordingly the present experiments have been carried out with the object of separating these lower members of unsaturated alcohols starting with a large quantity of sperm head oil. For these purposes, sperm head oil was converted into a mixture of methyl esters and free unsaponifiable matter by methanolysis, and the mixture was fractionally distilled. From the fraction boiling below 180°/15 mm. the unsaponifiable matter was separated and then acetylated. The acetates thus obtained were brominated, and the product was distilled so as to remove the saturated acetates as distillate, leaving the bromides of unsaturated acetates as residue. This was debrominated and reconverted into the unsaturated acetates, from which hexadecenyl acetate and tetradecenyl acetate were separated on fractionation. Saponification of the acetates yielded hexadecenol

(2) *Compt. rend.*, **183** (1926), 663; **185** (1927), 279.
(3) *J. Soc. Chem. Ind.*, **48** (1929), 365.
(4) *J. Soc. Chem. Ind., Japan*, **30** (1927), 527.
(5) This Bulletin, **10** (1935), 570.

and tetradecenol which, however, were contaminated with a small proportion of saturated alcohols. A complete removal of the latter was not attained in these experiments.

For the determination of the position of ethylenic linking in two alcohols, the acetates were oxidised with potassium permanganate in glacial acetic acid. Hexadecenyl acetate yielded *n*-heptoic acid $CH_3 \cdot (CH_2)_5 \cdot COOH$ and acetyl-hydroxynonoic acid $HOOC \cdot (CH_2)_7 \cdot CH_2O \cdot COCH_3$; hydroxynonoic acid liberated from its acetyl ester yielded, on further oxidation, azelaic acid $HOOC \cdot (CH_2)_7 \cdot COOH$. Tetradecenyl acetate yielded, on subsequent saponification of the ester in the oxidation products, *n*-nonoic acid $CH_3 \cdot (CH_2)_7 \cdot COOH$ and hydroxyvaleric acid $HOOC \cdot (CH_2)_3 \cdot CH_2OH$; the latter yielded on further oxidation glutaric acid $HOOC \cdot (CH_2)_3 \cdot COOH$. From these results the following constitutions were established:

Hexadecenol	$CH_3 \cdot (CH_2)_5 \cdot CH{=}CH \cdot (CH_2)_7 \cdot CH_2OH$,
Tetradecenol	$CH_3 \cdot (CH_2)_7 \cdot CH{=}CH \cdot (CH_2)_3 \cdot CH_2OH$.

According to the above constitutions, hexadecenol in sperm head oil corresponds to zoomaric acid ($\Delta^{9:10}$-hexadecenoic acid) which is of common occurrence in marine animal oils, and tetradecenol in sperm head oil corresponds to physeteric acid ($\Delta^{5:6}$-tetradecenoic acid) found in sperm oil. A similar relation exists between oleyl alcohol ($\Delta^{9:10}$-octadecenol) found in sperm oil and some other marine animal oils and oleic acid ($\Delta^{9:10}$-octadecenoic acid). It is, therefore, advisable to designate hexadecenol and tetradecenol in sperm head oil as zoomaryl alcohol and physeteryl alcohol respectively.

Experimental.

1. Separation of Hexadecenol. The same specimen of sperm head oil[6] as used for the separation of denticetic acid was employed for the present experiments. The oil was pressed at the room temperature to remove the solid portion, and the liquid portion was subjected to methanolysis by means of methanol containing sodium hydroxide. The product of methanolysis (10 kg.), consisting of the methyl esters and the free unsaponifiable matter, was distilled, the fraction boiling below 180°/15 mm. was separated and saponified, and the soap solution was treated with ether for the extraction of unsaponifiable matter. The yield of unsaponifiable matter was 357 g. It was acetylated by heating with acetic anhydride. The resulting acetates (410 g.) having saponification value 206.6 and iodine value (Wijs) 24.3 were dissolved in 4 l. of ether, and a little excess of bromine was gradually added with constant stirring under cooling with ice. The excess of bromine was removed from the ethereal solution by washing with sodium thiosulphate solution, and the ethereal solution was then washed with water and dehydrated. On removal of ether, the product of bromination was subjected to distillation. The rate of

(6) This Bulletin, **10** (1935), 570.

the distillation of saturated acetates became very slow at about 180°/2 mm. when the distillation was discontinued, and there was obtained 160 g. of residue consisting of the bromides of unsaturated acetates. It was dissolved in 250 c.c. of methanol, 160 g. of zinc powder was added, and the liquid was heated on the water-bath under a reflux condenser, while 250 c.c. of 5 N hydrogen chloride in methanol was gradually added. After heating for one hour, the insoluble residue was filtered off, the filtrate was diluted with a large quantity of water, and the debrominated product was extracted with ether. The insoluble residue was washed thoroughly with ether, and the washing was added to the main ethereal solution. After washing with water and subsequent removal of ether from the united ethereal solution, the residue was heated with acetic anhydride to regenerate acetates since it was found that the hydrolysis of acetates had taken place in the course of debromination with the formation of free alcohols. The acetates (97 g.) thus obtained was fractionally distilled up to 200°/15 mm., and the following fractions were separately collected.

Fraction	B.p. /15 mm.	Saponif. value	Iodine value	n_D^{20}	Yield (g.)
(1)	Below 160°	—	—	—	1.1
(2)	160–175°	215.7	91.1	1.4459	4.5
(3)	175–185°	209.2	87.1	1.4469	5.4
(4)	185–195°	200.3	84.3	1.4477	15.0
(5)	195–200°	195.2	82.2	1.4486	40.1
Residue and loss	—	—	—	—	30.9

The fraction (4) was subjected to a further fractionation, by which the portion boiling above 195°/15 mm. was separated. This was united with the fraction (5), and repeatedly fractionated, by which 12.2 g. of a fraction boiling at 195–198°/15 mm. and having the following constants was separated as hexadecenyl acetate $C_{18}H_{34}O_2$.

d_4^{15} 0.8760, d_4^{20} 0.8725, n_D^{15} 1.4596, n_D^{20} 1.4486, mol. refraction (based on the data at 15°) 86.70 (calc. for $C_{18}H_{34}O_2$ F_1: 86.51), saponif. value 197.5 (calc. 198.8), iodine value 83.2 (calc. 89.9).

Hexadecenol obtained by saponification of the acetate showed the following constants (Found: C, 79.91; H, 13.45. Calc. for $C_{16}H_{32}O$: C, 79.91; H, 13.42%).

d_4^{15} 0.8537, d_4^{20} 0.8503, n_D^{15} 1.4605, n_D^{20} 1.4584, mol. refraction (based on the data at 15°) 77.15 (calc. for $C_{16}H_{32}O$ F_1: 77.14), iodine value 93.6 (calc. 105.7).

The hydrogenation product of hexadecenol crystallised from 90% alcohol in lustrous laminae which showed acetyl value 197.1 (calc. for cetyl alcohol $C_{16}H_{34}O$: 197.4) and melted at 49.5–50° both alone or admixed with cetyl alcohol. On oxidising the hydrogenation product with chromic acid in glacial acetic acid, it yielded palmitic acid $C_{16}H_{32}O_2$; neutr. value 218.1 (calc. 219.0), m.p. and mixed m.p. 62–62.5°.

2. **Oxidation of Hexadecenyl Acetate.** Ten grams of hexadecenyl acetate was dissolved in 100 g. of glacial acetic acid, and 20 g. of powdered potassium permanganate was added in small portions. After heating for one hour on the water-bath under a reflux condenser,

the solution was diluted with water, and the oxidation products were extracted with a large quantity of ether. After a portion of the solvent had been distilled off, the ethereal solution was shaken with potassium carbonate solution which separated the acidic substances as their potassium salts from the neutral substances remaining in the ethereal solution. The aqueous solution containing potassium salts was acidified with hydrochloric acid, the liberated acidic substances were taken up with ether, and the ethereal solution was washed with water until the acidity of the washing became very faint. On removal of ether, there was obtained 6.5 g. of acidic substances. A comparatively low yield may be attributed to an incomplete oxidation with potassium permanganate or to the loss caused by washing the ethereal solution with water. These were distilled; 1.8 g. of a fraction (a) boiling below 185°/100 mm. was first separated, and then the distillation was carried out under a lower pressure, giving 3.1 g. of a fraction (b) boiling below 198°/5 mm.

The fraction (a) was redistilled, and a fraction boiling below 170°/100 mm. was collected. It was washed with a little water for the removal of the contaminated acetic acid, and the remaining liquid showed neutr. value 433.2 (calc. for $C_7H_{14}O_2$: 431.2) and n_D^{20} 1.4217, and was identified as *n*-heptoic acid by preparing its amide which, after being recrystallised from petroleum ether, melted at 94.5–95° both alone or admixed with *n*-heptoic acid amide[7] (Found: N, 10.70. Calc. for $C_7H_{15}ON$: N, 10.85%).

On subjecting the fraction (b) to a further fractionation, a fraction boiling at 200–204°/15 mm. was separated which was found to be acetyl-hydroxynonoic acid $C_{11}H_{20}O_4$.

d_4^{20} 1.0187, n_D^{20} 1.4462, mol. refraction 56.61 (calc. for $C_{11}H_{20}O_4$: 56.19), neutr. value 255.1 (calc. 259.6), saponif. value 509.4 (calc. 519.1).

Hydroxynonoic acid $C_9H_{18}O_3$ obtained by saponification of its acetyl derivative was a viscous oil having neutr. value 315.3 (calc. 322.2). Oxidation of hydroxynonoic acid with chromic acid in glacial acetic acid gave a solid product. It was taken up with ether, the ethereal solution was washed with water containing sodium chloride, and after distilling off ether from the ethereal solution the residue was recrystallised from water, yielding azelaic acid $C_9H_{16}O_4$ which had neutr. value 594.5 (calc. 596.5), m.p. 104–105°, and mixed m.p. 105–106°[8] (Found: C, 57.30; H, 8.50. Calc. for $C_9H_{16}O_4$: C, 57.41; H, 8.57%).

3. **Separation of Tetradecenol.** As described above, 97 g. of unsaturated acetates were fractionated, and five fractions (1)–(5) were separately collected. For the separation of tetradecenol, the fraction (2) and the portion boiling below 175°/15 mm. obtained by a repeated fractionation of the fraction (3) were combined and subjected to a further fractionation, and there was obtained 3.4 g. of a fraction boiling at 165–170°/15 mm. as tetradecenyl acetate $C_{16}H_{30}O_2$. It had the following constants.

d_4^{15} 0.8729, d_4^{20} 0.8694, n_D^{15} 1.4477, n_D^{20} 1.4457, mol. refraction (based on the data at 15°) 77.93 (calc. for $C_{16}H_{30}O_2$ $\overline{F}_1$: 77.28), saponif. value 218.2 (calc. 220.7), iodine value 92.7 (calc. 99.8).

Tetradecenol $C_{14}H_{28}O$ liberated from its acetate showed the following constants (Found: C, 79.29; H, 13.23. Calc. for $C_{14}H_{28}O$: C, 79.16; H, 13.30%).

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(7) The specimen used for the mixed melting point test was prepared in the following way: castor oil was first subjected to dry distillation, and a fraction corresponding to *n*-heptyl aldehyde was separated. The latter was oxidised into *n*-heptoic acid, which was then converted into the amide; m p. 94.5–95°.

(8) Azelaic acid used for the mixed melting point test was obtained by the ozonolysis of oleic acid.

d_4^{15} 0.8507, d_4^{20} 0.8473, n_D^{15} 1.4573, n_D^{20} 1.4553, mol. refraction (based on the data at 15°) 67.98 (calc. for $C_{14}H_{28}O$ $\overline{1}$: 67.91), iodine value 111.2 (calc. 119.6).

When hydrogenated, tetradecenol yielded a crystalline solid which on recrystallisation from 80% alcohol melted at 37–37.5°. The melting point is nearly the same as recorded for *n*-tetradecanol (38°).[9] On oxidising the hydrogenation product with chromic acid in glacial acetic acid, it yielded myristic acid $C_{14}H_{28}O_2$ which, after being recrystallised from 80% alcohol, showed neutr. value 244.2 (calc. 245.8), m.p. and mixed m.p. 53.5–54°.

4. **Oxidation of Tetradecenyl Acetate.** Tetradecenyl acetate (2.7 g.) was dissolved in 27 g. of glacial acetic acid, 6 g. of powdered potassium permanganate was added, and the solution was heated on the water-bath under a reflux condenser for 2 hours. Water was then added, the oxidation products were extracted with a large quantity of ether, and the ethereal solution was concentrated and shaken with potassium carbonate solution. By these treatments acidic substances were converted into their potassium salts and separated from the ethereal solution, while the neutral substances which escaped oxidation remained in the ethereal solution. The aqueous solution containing potassium salts was heated with the addition of potassium hydroxide on the water-bath in order to saponify the ester. The free acidic substances liberated on acidification with hydrochloric acid was once taken up with ether, the ethereal solution was washed with water containing sodium chloride, and then the ether was driven off. The acidic substances (2.2 g.) thus obtained were treated with a little water, yielding the aqueous solution and the insoluble portion.

The insoluble portion (1.2 g.) was distilled, and a fraction boiling below 195°/100 mm. was separated. It showed neutr. value 358.1 (calc. for $C_9H_{18}O_2$: 354.8) and n_D^{20} 1.4322. Its amide, when recrystallised from 50% alcohol, melted at 97.5–98°. The melting point was not lowered when the substance was admixed with varying proportions of a pure specimen of *n*-nonoic acid amide,[10] m.p. 98.5–99°.

Sodium chloride was added to the aqueous solution separated from the insoluble portion, and the solution was shaken with ether. On removal of ether from the ethereal solution, the residue was treated with petroleum ether, and the insoluble portion was separated which consisted of an oily liquid and had neutr. value 482.1 (calc. for hydroxyvaleric acid $C_5H_{10}O_3$: 475.2). This was subjected to oxidation with chromic acid in glacial acetic acid, and the product was collected by using ether. The residue obtained by distilling off ether was recrystallised from benzene, yielding crystals of m.p. 96–96.5°. The melting point was not lowered when the crystals were admixed with varying proportions of glutaric acid (m.p. 97.5–98°).

Summary.

Hexadecenol and tetradecenol have been isolated from the unsaponifiable matter of sperm head oil, and the acetates of these alcohols have been oxidised with potassium permanganate in glacial acetic acid. From the results of an examination of the oxidation products, the constitutions of these alcohols have been established as follows:

(9) "Beilsteins Handbuch der organischen Chemie", 4th Ed., I, 428.

(10) Prepared from *n*-nonoic acid which was obtained by the ozonolysis of oleic acid.

$\Delta^{9:10}$-Hexadecenol (zoomaryl alcohol) $CH_3\cdot(CH_2)_5CH{=}CH\cdot(CH_2)_7\cdot CH_2OH$

$\Delta^{5:6}$-Tetradecenol (physeteryl alcohol) $CH_3\cdot(CH_2)_7CH{=}CH\cdot(CH_2)_3\cdot CH_2OH$

It is thus seen that hexadecenol and tetradecenol in sperm head oil are the mono-ethylenic alcohols corresponding to zoomaric acid ($\Delta^{9:10}$-hexadecenoic acid) and physeteric acid ($\Delta^{5:6}$-tetradecenoic acid) respectively.

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HEXADECENOL IN SPERM BLUBBER OIL.*

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In a previous study on the unsaponifiable matter of sperm blubber oil by one of us (Toyama),[1] oleyl alcohol, cetyl alcohol and octadecyl alcohol were separated, and the presence of cholesterol in a small proportion was also indicated. Other minor components were, however, not closely studied; hexadecenol was not separated and it was thought that this alcohol could have been present, if any, only in an extremely small amount. We have now made a closer examination of the minor components of the unsaponifiable matter of sperm blubber oil. The present paper deals with the experimental results concerning hexadecenol.

The higher aliphatic alcohols are now being produced on industrial scale by the high pressure hydrogenation of the corresponding fatty acids or their esters, and find a wide application in the industrial field. On the other hand, sperm oil has recently attracted much interest owing to its high content of higher alcohols, and the methods of the separation of these higher alcohols from sperm oil have been much studied. A method is now being carried out on industrial scale in this country. Furthermore, it should be noted that the unsaturated higher alcohols, such as oleyl alcohol which is contained in sperm blubber oil in a large proportion, appear not to have been obtained as yet by the high pressure hydrogenation of the corresponding fatty acids or their

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* Translated from the Japanese text published in *J. Chem. Soc. Japan*, **56** (1935), 1077.

(1) *J. Soc. Chem. Ind., Japan*, **30** (1927), 527.

esters, and consequently sperm blubber oil seems to be the only important raw material of the unsaturated alcohols. Under these circumstances, it is desirable, also from the industrial point of view, to gain a fuller information on the unsaturated alcohols in sperm blubber oil.

In these experiments, the unsaponifiable matter was first prepared by heating the sperm blubber oil with barium hydroxide and water under pressure and by subsequent extraction of the product consisting of barium soaps and free unsaponifiable matter with acetone. The acetone extract thus obtained was, however, contaminated with a small amount of barium soaps and unsaponified oil. It was, therefore, refluxed with alcoholic potash to effect a complete saponification of the contaminated oil, after which the product was acidified with hydrochloric acid. The resulting unsaponifiable matter which was contaminated with free fatty acids was taken up with ether, the ethereal solution was washed with an aqueous solution of potassium hydroxide containing a little alcohol in order to remove the free fatty acids as their potassium soaps, and the unsaponifiable matter was obtained from the ethereal solution. The unsaponifiable matter (10 kg.) thus obtained was fractionally distilled, the fraction boiling below 188°/ca. 5 mm. was separated, and the solid portion was removed by cooling the fraction dissolved in acetone. The liquid portion was converted into acetates and fractionated. The higher fraction was removed, and the lower fraction was saponified to yield free alcohols, from which a further quantity of solid portion was removed on cooling the acetone solution. The liquid portion was subjected to a further fractional distillation, by which the fraction boiling below 200°/15 mm. was separately collected. This fraction still contained a considerable amount of saturated alcohols. For a further removal of saturated alcohols, it was converted into acetates and then brominated. The product was distilled so as to remove the saturated acetates as distillate, leaving the bromides of unsaturated acetates as residue which was then debrominated to regenerate the unsaturated acetates. These were saponified, and the free alcohols were subjected to a further distillation in order to remove the high boiling portions. Since the lower fraction was suspected to be contaminated with some hydrocarbons, it was treated with 85% methanol, the insoluble portion removed, and the soluble portion separated. After repeated fractionation there was obtained a fraction corresponding to hexadecenol. The actual yield was only 16 g., but the total quantity contained in the unsaponifiable matter used for these experiments would be far larger than the actual yield. The presence of tetradecenol was not ascertained in these experiments; it could have been present, if any, in a far smaller amount than hexadecenol.

The acetate of hexadecenol was oxidised with potassium permanganate in acetone. Among the oxidation products, *n*-heptoic acid $CH_3 \cdot (CH_2)_5 \cdot COOH$ and acetyl-hydroxynonoic acid $HOOC \cdot (CH_2)_7 \cdot CH_2O \cdot COCH_3$ were identified. Further oxidation of hydroxynonoic acid, obtained by saponification of its acetate, with chromic acid in acetic acid yielded azelaic acid $HOOC \cdot (CH_2)_7 \cdot COOH$. Hence, the constitution of hexadecenol is represented by the formula $CH_3 \cdot (CH_2)_5 \cdot CH=CH \cdot (CH_2)_7 \cdot CH_2OH$. It is thus seen that hexadecenol in sperm blubber oil is identical with zoomaryl alcohol ($\Delta^{9:10}$-hexadecenol) in sperm head oil.

Experimental.

1. **Separation of Unsaponifiable Matter.** Sperm blubber oil used for these experiments was procured from the Nihon Hogei K. K. (Japan Whaling Co., Ltd.) and had d_4^{25} 0.8735, n_D^{25} 1.4635, acid value 0.85, saponification value 123.8, iodine value (Wijs) 82.6 and unsaponifiable matter 38.98%. It deposited a large amount of crystalline solid at the room temperature. The unsaponifiable matter was separated in the following way: every 1 kg. of the oil was mixed with 400 g. of crystalline barium hydroxide (corresponding to an excess of 12%) and 1 l. of water, and the mixture was heated for one hour under 5–6 atm. in an autoclave. The product was taken out from the autoclave, squeezed for the removal of water as far as possible, then mixed with anhydrous sodium sulphate, cut into small pieces and extracted with acetone in an extractor. The acetone extract containing unsaponifiable matter was contaminated with a small amount of barium soaps and unsaponified oil, and on removal of acetone the residue was refluxed with an excess of alcoholic potash in order to effect a complete saponification. The product was then acidified with hydrochloric acid, and the unsaponifiable matter together with a small proportion of free fatty acids were taken up with ether. The ethereal solution was washed with an aqueous solution of potassium hydroxide containing a little alcohol, and the free fatty acids were converted into potassium soaps which were separated from the ethereal solution. The latter was thoroughly washed with water, and the solvent was removed by distillation. The yield of unsaponifiable matter was 10,120 g. (or 36.1%) from 28 kg. of the oil. It had d_4^{25} 0.8443, n_D^{25} 1.4572, acetyl value 186.8 and iodine value 73.9, and deposited a large amount of crystalline solid at the room temperature so that it was not mobile.

2. **Fractionation of Unsaponifiable Matter and Removal of Solid Portion.** The unsaponifiable matter obtained above was subjected to a fractional distillation. A batch of 530 g. was taken in each distillation, and 5 fractions were separately collected; fractions (1) and (2) were collected in an amount of 100 c.c. by volume, fraction (3) 200 c.c., fraction (4) 100 c.c., and fraction (5) consisted of the remainder of the distillate which was obtained by continuing the distillation until nearly nothing distilled further. The pressure was not maintained exactly at 5 mm. in each run, and consequently the boiling points given below were not estimated exactly in the same way in each run. The following results were obtained from 10,070 g. in total.

Fraction	B.p. / 5 mm.	Iodine value	Yield (g.)
(1)	Below 188°	51.8	1,600
(2)	188 - 190°	57.5	1,600
(3)	190 - 192°	68.4	3,190
(4)	192 - 195°	80.6	1,580
(5)	195 - 198°	96.8	1,680
Residue and loss	—	—	420

Fraction (1) was dissolved in 16 l. of 95% acetone, kept at 5–7° over a night, and the crystalline deposit formed was filtered off. It had iodine value 11.5, while the liquid portion (1,140 g.) obtained from the filtrate had iodine value 68.1. The latter was acetylated by heating with acetic anhydride, and the acetates having saponif. value 185.6 were distilled, yielding 829 g. of a fraction boiling below 212°/15 mm. This was saponified, and the free alcohols liberated were dissolved in 95% acetone as before and kept at 0° over a night. The solid portion was removed by filtration, and there was obtained 610 g. of the liquid portion from the filtrate which was then distilled, yielding 238 g. of a fraction boiling below 200°/15 mm. For a further removal of solid portion from this fraction it was dissolved in 95% acetone, cooled down to −10°, and the solid deposit was filtered off. The liquid portion (238 g.) obtained from the filtrate was then dissolved in 90% acetone, cooled down to −12°, and on removal of a further quantity of solid deposit, there was obtained 208 g. of liquid portion from the filtrate. It was distilled once more, and 160 g. of a fraction boiling below 200°/15 mm. and having iodine value 71.2 was separately collected.

3. **Separation of Hexadecenol.** The fraction described above, boiling below 200°/15 mm., was converted into the acetates. These (188 g.) were dissolved in 1.9 l. of ether, cooled down to −10°, and bromine (80 g.) in a slight excess was gradually added with constant stirring in the course of two hours. After standing for a short time, the excess of bromine was removed by washing with sodium thiosulphate solution, and then the ether was distilled off from the solution, giving 257 g. of the product of bromination which consisted of the unchanged saturated acetates and the bromides derived from unsaturated acetates. It was then subjected to distillation in order to drive off the saturated acetates. The distillation was continued up to 160°/2 mm., when the rate of distillation became very slow, and the operation was discontinued. Yield of the residual bromides 198 g. These were mixed with 200 g. of zinc powder, and 300 c.c. of methanol was added. The mixture was heated on the water-bath under a reflux condenser with the addition of 300 c.c. of 5 N hydrogen chloride in methanol in the course of 30 minutes, and after heating for 30 minutes more, the mixture was diluted with water. The oily substances separated were taken up with ether, and the ethereal solution was washed with water and then distilled. The debrominated products thus obtained were found to consist largely of free alcohols formed by the hydrolysis of acetates. They were reconverted into acetates by heating with acetic anhydride, and the latter distilled giving 116 g. of a fraction boiling below 215°/15 mm. The free alcohols obtained by saponifying this

fraction was distilled once more, giving 84 g. of a fraction boiling below 200°/15 mm. By these distillations, there was an indication of contamination of hydrocarbons in the fraction boiling below 200°/15 mm., especially in the lowest boiling portion. In an attempt to remove hydrocarbons the fraction boiling below 200°/15 mm. was shaken out with 900 c.c. of 85% methanol, kept at the room temperature over a night, and separated into the soluble and the insoluble portions. Each portion had the following constants, and the hydrocarbons seemed to be concentrated in the insoluble portion to a certain extent.

	Yield (g)	Iodine value	Acetyl value
Insoluble portion	17.4	95.1	192.4
Soluble portion	64.6	96.7	196.0

The soluble portion was distilled once more, giving 51 g. of a fraction boiling below 197°/15 mm. It was still contaminated with a small proportion of saturated compounds. It was dissolved in 370 c.c. of 90% acetone and cooled down to −20°, by which a small amount of solid deposit was formed. The liquid portion obtained from the filtrate was then subjected to a repeated fractionation, and 16 g. of a fraction boiling at 187–190°/15 mm. was finally separated as hexadecenol $C_{16}H_{32}O$.(2)

d_4^{15} 0.8534, n_D^{15} 1.4600, mol. refraction 77.11 (calc. for $C_{16}H_{32}O$ F_1: 77.14), iodine value 98.0 (calc. 105.7).

Hydrogenation of hexadecenol yielded cetyl alcohol $C_{16}H_{34}O$ which showed acetyl value 197.2 (calc. 197.4), m.p. and mixed m.p. 49.5° after recrystallisation from 95% alcohol. Hexadecenyl acetate $C_{18}H_{34}O_2$ obtained by heating hexadecenol with acetic anhydride had the following constants.

d_4^{15} 0.8760, n_D^{15} 1.4508, mol. refraction 86.73 (calc. for $C_{18}H_{34}O_2$ F_1: 86.51), saponif. value 196.8 (calc. 198.8), iodine value 83.5 (calc. 89.9).

4. **Oxidation of Hexadecenyl Acetate.** Ten grams of hexadecenyl acetate was dissolved in 100 c.c. of acetone, and the solution was heated on the water-bath under reflux condenser with the addition of 30 g. of powdered potassium permanganate in the course of 40 minutes, and the heating was continued for 30 minutes more. Water (250 c.c.) was then added, and a current of sulphur dioxide was passed into the solution until the excess of permanganate and the insoluble oxides of manganese disappeared completely. The solution was shaken with 1 l. of ether in order to extract the oxidation products, and the ethereal solution was then treated with potassium carbonate solution which dissolved out the acidic oxidation products as their potassium salts, leaving the neutral substances in ethereal solution. On removal of ether, there remained 3.2 g. of neutral substances. The aqueous solution containing potassium salts was acidified with hydrochloric acid, the acidic substances liberated were taken up with ether, the ethereal solution

(2) The fraction boiling below 187°/15 mm. was obtained with a yield of 15 g., and had acetyl value 196.1. Though the comparatively low acetyl value might be attributed to a contamination of hydrocarbons, tetradecenol was considered to be present, if any, only in a far smaller amount than hexadecenol in sperm blubber oil.

was washed with water containing sodium chloride, and on distilling off ether from the solution, there was obtained 7.7 g. of acidic substances as an orange yellow liquid. It was fractionated; the fraction (a) boiling below 160°/100 mm., 1.6 g., was first separated, then the fractionation was continued under a lower pressure, and after the fraction boiling below 160°/5 mm., 2.0 g., was set apart, the fraction (b) boiling at 160–190°/5 mm., 2.0 g., was separated. On refractionation of the fraction (a), the portion boiling below 160°/100 mm. was separated which had neutr. value 431.5 (calc. for $C_7H_{14}O_2$: 431.2). The amide prepared from it melted at 94-94.5° after recrystallisation from petroleum ether and no depression of melting point was observed when the substance was admixed with a pure specimen of *n*-heptoic acid amide.(3)

The fraction (b) had neutr. value 269.0 and saponif. value 537.5, and was thought to consist mainly of acetyl-hydroxynonoic acid $C_{11}H_{20}O_4$ (neutr. value 259.6 and saponif. value 519.1). The free hydroxy-acid obtained on saponification of the acetate was purified by washing with petroleum ether, yielding hydroxynonoic acid $C_9H_{18}O_3$ as a faintly yellow, viscous oil having neutr. value 329.2 (calc. 322.2). Acetyl-hydroxynonoic acid regenerated by heating the free hydroxynonoic acid with acetic anhydride showed neutr. value 261.2 and saponif. value 513.5. For a further oxidation of hydroxynonoic acid, 0.8 g. of the substance was dissolved in 30 c.c. of glacial acetic acid, and the solution was heated with the addition of 5 g. of chromic acid on the water-bath under reflux condenser for two hours. The oxidation products were once taken up with 400 c.c. of ether, and after the ethereal solution being washed with water, the ether was removed by distillation, yielding a crystalline residue from which azelaic acid $C_9H_{16}O_4$ was obtained on recrystallising from water; neutr. value 591.2 (calc. 596.5), m.p. and mixed m.p. 105-106°.(4)

Summary.

Hexadecenol has been separated, in a very small yield, from the unsaponifiable matter of sperm blubber oil, and its constitution has been established as $CH_3\cdot(CH_2)_5\cdot CH{=}CH\cdot(CH_2)_7\cdot CH_2OH$. Hence, hexadecenol in sperm blubber oil is proved to be identical with zoomaryl alcohol ($\Delta^{9:10}$-hexadecenol) previously found in sperm head oil.

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(3) *n*-Heptyl aldehyde was separated from the product of dry distillation of castor oil. It was then oxidised into *n*-heptoic acid, from which the amide was prepared; m.p. 94.5–95°.

(4) Azelaic acid used for the mixed melting point test was prepared by the ozonolysis of oleic acid.

ATTEMPTED FORMATION OF RINGS ATTACHED TO THE *p*-POSITIONS OF THE PHENYL GROUPS IN 2,2′-DIPHENYLDIPHENYL.

By Shin-ichi SAKO.

Received September 5th, 1935. Published December 28th, 1935.

In a previous communication dealing with the relative ease of formation of carbon rings,[1] it was pointed out that the difficulty attending formation of large carbon rings should be attributed mainly to free rotation of atoms constituting open carbon chains, and consequently that this difficulty should be reduced by inhibiting free rotation. One of the examples cited in support of this view was that which was encountered in the facile formation of seven-membered rings attached to the 2,2′-positions of diphenyl. The present paper deals with the case of 2,2′-diphenyldiphenyl (I), in the *p*-positions of the phenyl groups of which are present suitable substituents through which cyclization may be effected.

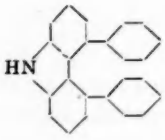
Although the number of carbon atoms separating the *p*-substituting atoms in the phenyl groups in 2,2′-diphenyldiphenyl exceed that separating the 2,2′-substituting atoms in diphenyl by as many as eight, it is clear that, as a result of inhibition of free rotation, the relative position of the *p*-substituting atoms in the former compound is altered only by free rotation of the benzene nuclei around the common axis of the central diphenyl system, a condition which is precisely the same in the case of 2,2′-substituting atoms in diphenyl. Thus, in regard to one of the main factors which determine the ease of ring formation, there is a close similarity between the 2,2′-positions and the *p*-positions of the phenyl groups. We are however not as yet certain whether substituting atoms in the *p*-positions of the phenyl groups in 2,2′-diphenyldiphenyl can approach each other or not, for, in order to do so, the compound will have to assume a strained configuration. It should be noted that in this case the valency angle will have to be increased in order to bring the *p*-substituting atoms close together, just as Baeyer[2] has erroneously supposed to be the case in alicyclic rings composed of six carbon atoms and more, but in the present case the condition is altogether different and there seems to be no means whereby strain can be relieved.

On the other hand, although the supposed condition of 2,2′-diphenyldiphenyl molecule involves strain, this is not large (here it is assumed that the

(1) This Bulletin, **9** (1934), 41.
(2) *Ber.*, **18** (1885), 2277.

valency deflection is possible only in the planes in which the benzene nuclei lie[3]). Further, a fact from which we may assume that there is a possibility of the *p*-substituting atoms coming close together is to be found in the ready formation of 4,5-diphenyl carbazole (II)[4] and 4,5-diphenyldiphenylene oxide (III)[5] from 2,2′-diamino-6,6′-diphenyldiphenyl, since, as has been shown some time ago,[3] the closure of five-membered rings in these substances must necessarily be accompanied by the two atoms in question being in close proximity.

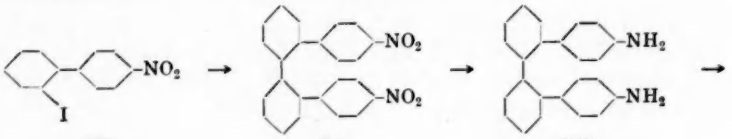
(I)



(II)

(III)

With these considerations in mind, the possibility of effecting cyclization in 2,2′-bis-(*p*-nitrophenyl)-diphenyl (V), 2,2′-bis-(*p*-aminophenyl)-diphenyl (VI), and 2,2′-bis-(*p*-halogenophenyl)-diphenyl (VII) has been investigated. 4′-Nitro-2-iododiphenyl can be obtained from 4′-nitro-2-aminodiphenyl, and the compound has been treated with copper powder to yield (V), which has been converted successively into (VI) and (VII).



(IV) (V) (VI)

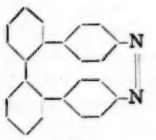
(VII) (VIII)

The yield of (V) has been found to be unexpectedly small. After a large number of comparative experiments, it has been found that the best yield (53% of the theoretical) is obtained when the quantity of copper powder is 1.4 times the theory, a larger amount giving a lower yield. The rather poor

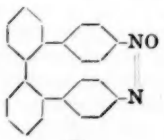
(3) This Bulletin, **9** (1934), 63–64.
(4) This Bulletin, **9** (1934), 70.
(5) This Bulletin, **9** (1934), 72.

yield seems due mainly to the reducing action of copper powder on the nitro-groups, for, in addition to (V), there is also produced a small quantity of a crystalline substance which appears to have the constitution (VIII). Search has naturally been made for the compound (IX) amongst the products, as it has been thought possible that, if the compound (VIII) is producible by the condensation of (IV) with (V) as would be supposed most probable, the compound (IX) may be produced from (V) alone, since, in general, combination of two atoms by an intramolecular reaction leading to a ring compound takes place more readily than that by an intermolecular one, provided of course that in the former case the atoms can approach each other easily. No crystalline substance other than (V) and (VIII) has however been isolated. It is possible that even though the compound (IX), the structure of which is not a stable one, is produced during the reaction, it cannot survive at such a high temperature as employed in this reaction.

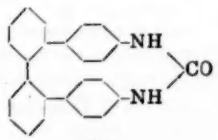
The comparison of the compounds (V), (VI), and (VII) respectively with 2,2′-dinitro-, 2,2′-diamino-, and 2,2′-dihalogeno-diphenyl shows at once that relative positions of the nitro-groups, the amino-groups, and the halogenoradicals in both series of compounds are altered in exactly the same way as already mentioned, and therefore if the methods such as those used for producing (i) phenazone[6] or phenazone oxide[7] from 2,2′-dinitrodiphenyl, (ii) 2-keto-2,3-dihydrodiphenimidine[8] from 2,2′-diaminodiphenyl and urea, (iii) carbazole[9] from 2,2′-diaminodiphenyl, (iv) diphenylene[10] from 2,2′-dibromodiphenyl can be applied to the compounds (V), (VI), and (VII), the result would be the formation of large ring compounds (IX), (X), (XI), (XII) and (XIII).



(IX)



(X)



(XI)

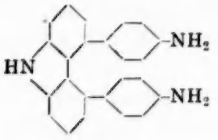
(XII)

(XIII)

(6) Täuber, *Ber.*, **24** (1891), 3085.
(7) Ullmann and Dieterle, *Ber.*, **37** (1904), 23.
(8) Niementowski, *Ber.*, **34** (1901), 3330.
(9) Täuber, *Ber.*, **24** (1891), 200.
(10) Dobbie, Fox, and Gauge, *J. Chem. Soc.*, **99** (1911), 683.

The strain in substances such as the hypothetical (XII) and (XIII) would undoubtedly be very large, and indeed with a Kekulé nucleus such formulæ can not be constructed. As a matter of fact, 2,2′-bis-(*p*-bromophenyl)-diphenyl and 2,2′-bis-(*p*-iodophenyl)-diphenyl (VII), on treatment with metallic sodium in absolute ether, gives 2,2′-diphenyldiphenyl (I) as the only crystalline product, and no reaction occurs when 2,2′-bis-(*p*-aminophenyl)-diphenyl is heated with hydrochloric acid at high temperatures.

In the case of hypothetical substances (IX), (X) and (XI), however, there appears to be less reason for instability, and if the nitrogen atoms in the compounds (V) and (VI) can only come close together, they may pass into the respective compounds (IX), (X), and (XI). In practice, however, it has been found that such cyclization cannot be effected. Whether this failure is due to the impossibility of bringing the nitrogen atoms close together or to the instability of the hypothetical rings, it is impossible at present to say, but if due to the former cause, it is possible that, in a compound such as (XIV) in which the two amino-groups would be in close proximity, cyclization reactions similar to those which take place in 2,2′-diaminodiphenyl as well as in *o*-phenylenediamine can be applied. It is proposed to investigate the possibility of ring formation in this or similarly constituted compounds.



(XIV)

Experimental.

4′-Nitro-2-aminodiphenyl hydrochloride. Scarborough and Waters,[11] by the nitration of 2-acetamidodiphenyl, obtained 4′-nitro-2-acetamidodiphenyl in 44 per cent. yield. The following method, which is an improvement of theirs, gave 78 per cent. yield.

To a solution of 53 g. of 2-acetamidodiphenyl in 53 c.c. of acetic acid and 106 c.c. of conc. H_2SO_4 was added at 0–2°C. a mixture of 15 c.c. of fuming HNO_3 (d=1.51) and 53 c.c. of acetic acid with stirring. About one hour was required for the addition of the mixed acid. After one more hour's agitation, the mixture was poured on ice, when the product formed a faintly yellow syrup which solidified after a time. The dried crude product weighed 63 g. On crystallization from chloroform, it gave light-yellow thin needles melting at 193°. The yield of pure 4′-nitro-2-acetamidodiphenyl was 50 g.

The acetyl compound was hydrolysed with moderate ease by alcoholic HCl and with difficulty by alkali. As the action of the 10 per cent. alcoholic HCl employed by Scarborough and Waters[11] proved too weak, the hydrolysis was conducted as follows: a suspension of 70 g. of 4′-nitro-2-acetamidodiphenyl in a mixture of 140 c.c. each of EtOH and conc. HCl was refluxed on the water bath for 90 minutes. The original substance disappeared in 15 minutes to be followed after a time by the separation of the crystalline

(11) *J. Chem. Soc.*, **1927**, 95.

4-nitro-2-aminodiphenyl hydrochloride. After cooling the crystals were collected and washed with 20 per cent. HCl solution (Found: Cl, 13.94. Calc. for $C_{12}H_{11}O_2N_2Cl$: Cl, 14.16%). The dried crystals weighed 65 g. The mother liquor, on concentration, gave a second crop, 2.8 g. The hydrochloride readily loses HCl either on heating or on washing with water, showing that it is a weak base.

4'-Nitro-2-iododiphenyl (IV). A mixture of 68 g. of 4'-nitro-2-aminodiphenyl hydrochloride, 100 c.c. of conc. HCl, and 80 g. of cracked ice was, with external cooling by ice, treated with 20.7 g. of solid sodium nitrite with stirring. The diazotized solution was filtered if necessary, treated with a solution of 60 g. of potassium iodide, and allowed to stand for three days until completion of the reaction (the decomposition by heating on the water bath somewhat lowers the yield of the iodo-compound). The crude iodo-compound thus precipitated, 89.7 g., was dissolved in ether and shaken with a KOH solution. After the removal of the ether, the residue was distilled in vacuum. It had b p. 203°/5 mm. On crystallization from EtOH, beautiful yellow needles melting at 100–101.5° separated. The yield of the purified substance was 64.6 g. (Found: C, 44.2; H, 2.7. Calc. for $C_{12}H_8O_2NI$: C, 44.3; H, 2.5%). 4'-Nitro-2-iododiphenyl is very easily soluble in boiling EtOH and sparingly so in the cold.

4'-Amino-2-iododiphenyl, its hydrochloride and the acetyl derivative. A hot solution of 10.8 g. of 4'-nitro-2-iododiphenyl in 100 c.c. of EtOH was mixed with 27 g. of $SnCl_2 \cdot 2H_2O$ and 33 c.c. of conc. HCl, and heated on the water bath for 15 minutes, at the end of which the yellow colour of the original substance had disappeared. The solution was concentrated to one half the original bulk, and, while still hot, diluted with 100 c.c. of water, when 4'-amino-2-iododiphenyl hydrochloride separated at once as colourless needles which were collected and washed with EtOH-water. The hydrochloride thus obtained was pure and weighed 10.6 g. It can be crystallized from EtOH or EtOH-water (Found: Cl, 10.60. Calc. for $C_{12}H_{11}NCl$: Cl, 10.70%).

The free base was obtained as follows: the hydrochloride obtained above was shaken with a sodium hydroxide solution and ether, and the ethereal layer evaporated up. The residual syrup resisted all attempts at crystallization. It was therefore purified by vacuum distillation (Found: I, 43.20. Calc. for $C_{12}H_{10}NI$: I, 43.02%).

The gummy free base on acetylation gave the crystalline acetyl derivative: on treatment of a conc. ethereal solution of 4'-amino-2-iododiphenyl with the calculated quantity of acetic anhydride, 4'-acetamido-2-iododiphenyl separated in colourless needles after a short time. It had m.p. 162–163°C. (Found: I, 37.49. Calc. for $C_{14}H_{12}ONI$: I, 37.66%).

The action of copper powder on 4'-nitro-2-iododiphenyl. Formation of 2,2'-bis-(*p*-nitrophenyl)-diphenyl (V) and 4-(*o*-iodophenyl)-4'-[*o*-(*p'*-nitro-*o*-diphenylyl)-phenyl]-azobenzene (VIII). As stated in the introduction the preparation of 2,2'-bis-(*p*-nitrophenyl)-diphenyl from 4'-nitro-2-iododiphenyl present unexpected difficulties, and, in spite of the many experiments made under a great variety of conditions, no more than a 50 per cent. yield could be obtained. The best result was obtained as follows.

2,2'-Bis-(p-nitrophenyl)-diphenyl (V). Copper powder (1.8 g.) prepared by the method of Piccard and Larsen[12] was added with stirring to 6.5 g. of 4'-nitro-2-iododiphenyl which was heated in an oil bath at 220-225°, and the heating and agitation continued for 80 minutes. After cooling, the solidified mass was extracted with 700 c.c. of C_6H_6. The

(12) *J. Am. Chem. Soc.*, **39** (1917), 2007.

extract was treated with animal charcoal and concentrated until, while heating, the crystals began to separate (about 180 c.c.). The yellow thin needles thus obtained, 2.1 g., was almost pure 2,2′-bis-(*p*-nitrophenyl)-diphenyl. The pure substance obtained by crystallization from benzene melted at 290° (Found: N, 7.2. Calc. for $C_{24}H_{16}O_4N_2$: N, 7.1%). By a couple of analyses on carbon and hydrogen, it was shown that the dinitro-compound is one of those rare organic compounds which do not give the correct figure for carbon, although a good result was obtained for the hydrogen content. About 100 c.c. of boiling benzene is required to dissolve 0.5 g. of this compound.

4-(o-Iodophenyl)-4′-[o-(p′-nitro-o-diphenylyl)-phenyl]-azobenzene (VIII). This substance was contained in the mother liquor of the yellow needles of 2,2′-bis-(*p*-nitrophenyl)-diphenyl described above. On concentration of this solution to about 10 c.c., 2,2′-bis-(*p*-nitrophenyl)-diphenyl (V), 0.14 g., separated, which was filtered off. The filtrate was evaporated off and the residue, after the removal of the alcohol-soluble part by extraction with EtOH, crystallized from 4 c.c. of benzene, inoculation being desirable if possible. The orange crystals of (VIII) thus obtained weighed 0.10 g. It happened at times that the orange crystals were contaminated with the yellow needles of (V). The mechanical separation of the two substances could be effected fairly completely by means of decantation, if proper care was taken that the orange crystals of (VIII) are made to grow large enough. A fact which should be noted in this connection is that, although the orange compound (VIII) used to separate from C_6H_6 in a compact granular form, it crystallized at times in short prisms and rarely in thin needles, and that these forms were capable of coexistence in benzene. The purified substance (VIII) melted, irrespective of crystalline forms, at 312–313° (Found: C, 64.8; H, 3.9; N, 6.7; I, 18.8. Calc. for $C_{36}H_{24}O_2N_3I$: C, 65.8; H, 3.7; N, 6.4; I, 19.3%). Rast's method for molecular weight determination could not be applied because of its slight solubility in camphor. On heating the powdered orange compound with a mixture of stannous chloride, conc. HCl, and acetic acid it disappeared slowly forming a colourless solution. This was probably the indication that the molecule was cleaved at the double bond to give the two amines, a reaction characteristic of an azo-compound. The substance is insoluble or very slightly soluble in usual organic solvents. Ten c.c. of boiling benzene dissolves about 0.1 g. of the orange crystals.

2,2′-Bis-(*p*-aminophenyl)-diphenyl (VI). This substance can be obtained by the reduction of 2,2′-bis-(*p*-nitrophenyl)-diphenyl (V) either with stannous chloride or with sodium sulphide.

Dry HCl was passed into a mixture of 5.3 g. of powdered 2,2′-bis-(*p*-nitrophenyl)-diphenyl, 2.7 g. of stannous chloride, and 150 c.c. of acetic acid, and the mixture heated on the water bath at 60–70°C. The sparingly soluble dinitro-compound slowly disappeared to be replaced by the voluminous, powdery double salt. As the mixture became very thick, frequent shaking was necessary. Heating was continued for some hours till the complete disappearance of the dinitro-compound, HCl being passed in all the time. After cooling, the fine bluish precipitate was collected, dissolved in 150 c.c. of water, treated with an excess of KOH solution, and the liberated base dissolved in ether. On removal of ether, the residue completely crystallized, which was distilled under reduced pressure. It had b.p. 290°/5 mm. The distillate was dissolved in boiling EtOH (36 c.c.), concentrated to about 18 c.c., and allowed to stand for crystallization. Inoculation was found often necessary. The large colourless crystals, 3.9 g., melted at 163-164°C. (Found: N, 8.6. Calc. for $C_{24}H_{20}N_2$: N, 8.3%). By concentration of the mother liquor, some more crystals separated, and the yield was quantitative.

The reduction of the dinitro-compound (V) with sodium sulphide was carried out as follows: a mixture of 2 g. of (V), 7.5 g. of sodium sulphide, 90 c.c. of EtOH, and 30 c.c. of H_2O was refluxed for three hours. The original substance disappeared in 30 minutes. On concentration of the reaction mixture to a small bulk, followed by the addition of water, an oil separated, which solidified at once. It was crystallized from EtOH. The crystals thus formed melted, either alone or when mixed with the diamino-compound obtained by the stannous chloride method described above, at 163–164°C.

2,2'-Bis-(*p*-iodophenyl)-diphenyl (VII). A suspension of 1.7 g. of 2,2'-bis-(*p*-aminophenyl)-diphenyl (VI) in 33 g. of 8 per cent. HCl solution was gently heated with agitation, when the difficultly soluble hydrochloride was deposited in needles. It was then cooled in ice and treated with 0.76 g. of sodium nitrite with agitation. After an hour's agitation, a clear solution resulted, which was treated with a solution of 2.4 g. of KI. It was then allowed to stand at ordinary temperature for two hours and finally heated at 50°C. The brown precipitate thus obtained was dissolved in ether, shaken with a KOH solution, and the ether removed. The residue, 2.6 g., was purified first by vacuum distillation and then by two crystallizations from C_6H_6–EtOH. It was obtained in yellow needles melting at 205–206°C. (Found: I, 44.4. Calc. for $C_{24}H_{16}I_2$: I, 45.5%). It is readily soluble in C_6H_6, less so in ether, and very difficultly soluble in EtOH.

2,2'-Bis-(*p*-bromophenyl)-diphenyl (VII). 2,2'-Bis-(*p*-aminophenyl)-diphenyl (1.7 g.) was gently heated with a 5 per cent. HBr solution. The clear solution thus obtained, on cooling with ice water, separated the dihydrobromide in needles. The latter, on treatment with a solution of 0.76 g. of sodium nitrite, disappeared in a short time. To the bisdiazonium bromide solution was added cuprous bromide, which was prepared by boiling a mixture of 1.26 g. of $CuSO_4 \cdot 5H_2O$, 0.40 g. of copper powder, 2.28 g. of anhydrous NaBr, 0.60 g. of conc. H_2SO_4, and 10 c.c. of water for some hours. The reaction mixture was allowed to stand for decomposition at ordinary temperature. The decomposition proceeded very slowly. After one week, it was heated at 50°, and the precipitated substance collected and extracted with ether. The ether was removed and the residue, on distillation under reduced pressure, gave a crystalline distillate (0.55 g.), which was twice recrystallized from EtOH (10 c.c.). The almost colourless needles thus obtained had m.p. 170–171°C. (Found: Br, 34.0. Calc. for $C_{24}H_{16}Br_2$: Br, 34.5%).

Instead of leaving, as described above, the bis-diazonium bromide solution at ordinary temperature, when it was heated at 50–60°, the decomposition was complete in one hour, but the product was contaminated with a larger quantity of impurities which rendered the purification difficult. In any case, the yield of the desired substance was far from being satisfactory.

The action of sodium on 2,2'-bis-(*p*-iodophenyl)-diphenyl. A solution of one gram of 2,2'-bis-(*p*-iodophenyl)-diphenyl in 150 c.c. of absolute ether was heated under reflux in a water bath at 45° with a large excess of finely divided sodium metal, with constant stirring (mercury seal). The separation of sodium iodide was noticeable after 20 hours' heating. The yellow colour of the solution gradually disappeared. After 63 hours' heating, it was filtered and the filtrate evaporated off. The residue which consisted of beautiful colourless crystals was dissolved in EtOH, treated with animal charcoal to remove a trace of an amorphous matter and the filtrate concentrated to a few c.c. The colourless crystals thus separated melted at 117–118°C. and found by the

mixed melting point method to be identical with 2,2'-diphenyldiphenyl made from 2-iododiphenyl.[13]

The action of metallic sodium on 2,2'-bis-(*p*-bromophenyl)-diphenyl. A solution of 0.4 g. of 2,2'-bis-(*p*-bromophenyl)-diphenyl in 100 c.c. of absolute ether was refluxed in a water bath at 45° for 100 hours with stirring. It was then filtered and the ether removed. The partly solidified residue was collected on a filter, washed first with EtOH and then with petroleum ether. The almost colourless needles thus obtained, 0.21 g., on crystallization from EtOH gave slender needles which proved to be the original dibromo-compound (mixed m.p.). The oily filtrate and the washings were united and the solvents removed. The residual gummy substance persistently resisted crystallization, but when seeded with a crystal of 2,2'-diphenyldiphenyl[13] prepared from 2-iododiphenyl, gradual increase of the crystals was observed, showing the presence of the same substance among the products. That some of the dibromo-compound was acted on by sodium was further shown by the fact that the aqueous solution of the solid separated from the original ethereal solution, on treatment with HNO_3 and $AgNO_3$, deposited AgBr.

Attempts to prepare the hypothetical large ring compounds (IX) and (X). As already described on p. 591, the action of sodium sulphide on 2,2'-bis-(*p*-nitrophenyl)-diphenyl (V) gave rise to the diamino-compound (VI), and not to the cyclic azoxy-compound (X). Another method of preparation of azoxy-compounds, namely, the use of alkaline arsenite[14] as the reducing agent was also attempted, but with indifferent success. Thus, although 2,2'-bis-(*p*-nitrophenyl)-diphenyl (0.5 g.), As_2O_3 (0.5 g.), NaOH (0.6 g.), H_2O (3 c.c.), and toluene (3.0 c.c.) were heated together in an oil bath at 145–160° for 40 hours with stirring, no change occurred, the original substance being recovered almost unchanged (in this reaction, in order to facilitate the reaction, toluene was used as solvent for the dinitro-compound which does not melt at the temperature). The use of alkaline stannite solution in an attempt to obtain the azo-compound (IX)[15] was also a failure.

The action of heat on 2,2'-bis-(*p*-aminophenyl)-diphenyl (VI) hydrochloride. 2,2'-Bis-(*p*-aminophenyl)-diphenyl (VI) and dil. HCl were heated in a sealed tube at high temperatures, but the only crystalline substance isolable was the unchanged diamino-compound.

The action of urea on 2,2'-bis-(*p*-aminophenyl)-diphenyl (VI). 2,2'-Bis-(*p*-aminophenyl)-diphenyl (VI) was heated either with urea alone or with a mixture of urea and *m*-cresol at varied temperatures. The liberation of ammonia gas was observed, but the reaction seemed to be a deep-seated one and no crystalline product could be isolated.

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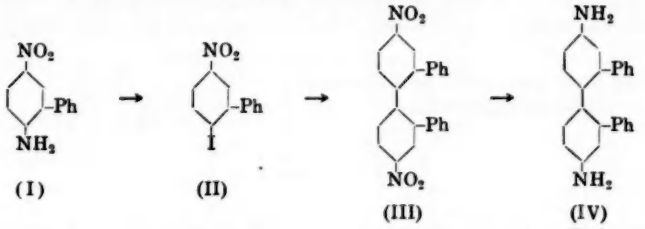
(13) Bowden, *J. Chem. Soc.*, **1931**, 1112.
(14) Loesner, *J. prakt. Chem.*, (2), **50** (1894), 564.
(15) Witt, *Ber.*, **18** (1885), 2912.

THE SYNTHESIS OF 2,2′-DIPHENYLBENZIDINE.

By Shin-ichi SAKO.

Received September 5th, 1935. Published December 28th, 1935.

The synthesis of 2,2′-diphenylbenzidine has been carried out in connection with the other diamino-derivatives[1] of 2,2′-diphenyldiphenyl prepared in this laboratory. The starting substance employed for this synthesis is 2-amino-5-nitro-diphenyl (I) which has been obtained along with 2-amino-3-nitro-diphenyl in the nitration[2] of 2-acetamidodiphenyl. 2-Amino-5-nitro-diphenyl has been converted into 5-nitro-2-iododiphenyl (II) in the usual way, and the latter treated with copper powder to yield 4,4′-dinitro-2,2′-diphenyldiphenyl (III) which, on reduction, gives 2,2′-diphenylbenzidine (IV).



Experimental.

5-Nitro-2-iododiphenyl (II). 2-Amino-5-nitrodiphenyl (I) (21.4 g.) was dissolved in 120 c.c. of conc. H_2SO_4 at ordinary temperature with stirring. The vessel was surrounded by ice water and the solution diluted with 40 g. of ice. With vigorous stirring, 7.2 g. of sodium nitrite were added at once. After some time 60 g. of ice was added in three portions with an interval between each addition. It was finally diluted with a large quantity of ice, filtered, and treated with a solution of 19 g. of potassium iodide in the cold. The iodo-compound separated in an oil which solidified slowly. The crude product, 32 g., was dissolved in ether, and the solution filtered to remove some insoluble matter, shaken with a potassium hydroxide solution and dried. The ether was then evaporated off and the residue distilled under reduced pressure. It had b.p. 191–192°/4 mm. Recrystallized from MeOH it formed light-yellow, long needles melting at 114°C (Found: I, 38.73. Calc. for $C_{12}H_8O_2NI$: I, 39.05%). The yield of the pure substance was 26 g.

4,4′-Dinitro-2,2′-diphenyldiphenyl (III). To 63 g. of 5-nitro-2-iododiphenyl heated in an oil bath at 215–225° was added during 10 minutes 45 g. of copper powder prepared by the method of Piccard and Larsen[3] with stirring, and the mixture heated 20 minutes

(1) This Bulletin, **9** (1934), 70; **10** (1935), 585.
(2) This Bulletin, **9** (1934), 65.
(3) *J. Am. Chem. Soc.*, **39** (1917), 2007.

more. The cooled mass was extracted with a large quantity of boiling benzene. After the removal of benzene, the residue was purified by vacuum distillation. It boiled at 290°/4 mm. On crystallization from benzene, yellow crystals melting at 218–219°C. separated (Found: N, 7.4. Calc. for $C_{24}H_{16}O_4N_2$: N, 7.1%). The yield was 27 g. It is moderately soluble in boiling benzene, and difficultly soluble in cold benzene and hot acetone.

2,2′-Diphenylbenzidine (IV). A suspension of 22 g. of powdered 4,4′-dinitro-2,2′-diphenyldiphenyl (III) in a solution of 100 g. of stannous chloride in 290 c.c. of acetic acid containing dry HCl was heated on the water bath for 8 hours with frequent shaking, HCl being led in all the time. Frequent shaking was necessary because the unchanged dinitro-compound which subsided was apt to be covered by the reaction product which, being almost insoluble, began to separate soon after the start. When the reaction was over, the precipitated double salt was collected, dissolved in 1100 c.c. of water, and made alkaline with a solution of KOH (60 g.). The free base which solidified at once was filtered, dissolved in ether and the solution filtered. The solvent was then removed and the residue, 18 g., on two crystallizations from EtOH, gave large crystals melting at 151–152°C. (Found: N, 8.7. Calc. for $C_{24}H_{20}N_2$: N, 8.3%). The separation of the crystals from the alcoholic solution was very slow. Its solution darkens in colour fairly quickly.

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A RESEARCH ON THE ABSOLUTE SINGLE POTENTIAL OF THE ELECTRODE.

By K. HIROTA and T. MURATA.

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"The absolute single potential" of an electrode determined by the electrocapillary curve and the drop mercury electrode has been subjected to various objections.[1] The potential across the Helmholz double layer might vanish at the maximum of electrocapillary curve, while the potential due to selective adsorption would persist. The latter effect may be neglected for the drop mercury electrode in the case of rapid flow of mercury; still we are not sure that the potential across the double layer vanishes in this case. We have tried the method described below by which the point of maximum interface tension is determined by means of a rapid jet of mercury into the solution.

(1) Frumkin, *Ergebnisse der exakten Naturwiss*, **7** (1928), 239. "Handbuch der Experimentalphysik, XII Elektrochemie," 2. Teil, 368.

Our method is based upon the following observations: the height of a mercury jet ejected upward through a small nozzle into a solution depends upon the electrical potential applied between the solution and the mercury; and the rate of the mercury flow is practically independent of the potential. It follows that the mercury is imparted with a constant kinetic energy as it leaves the nozzle. The kinetic energy is partly converted into the surface work which depends on the interface tension at the moment it spreads out into small mercury drops, and the rest of the energy determines the height of the mercury jet. The mininum in height should then correspond to the maximum interface tension.

The apparatus used is illustrated in Fig. 1. The mercury was allowed to flow down from a wide vessel and was ejected through an orifice of 0.08 mm.

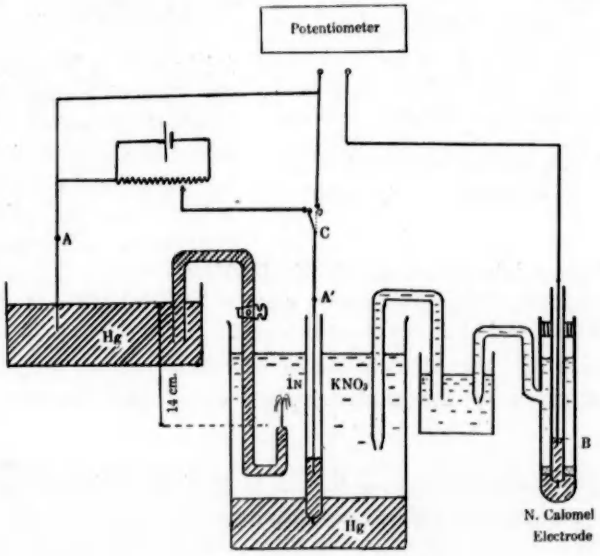

Fig. 1.

diameter into a normal potassium nitrate solution. The mercury head was practically constant during the experiment. The potential varying from zero to 1.5 volts was applied between A and A′, the corresponding potential of mercury jet against a normal calomel electrode B being measured by means of a potentiometer inserted between A and B. The height of the jet was measured with a microcathetometer accurately within 1/100 mm.

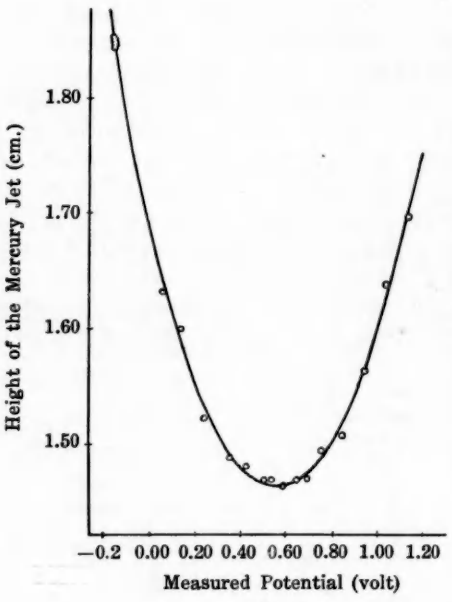

Fig. 2.

The height of the jet was plotted against the measured potential difference between the mercury jet and the normal calomel electrode. One of the series of measurements is shown in Fig. 2. A crowd of points on the upper part of the left branch of the curve shows measurements made in the absence of the applied potential (effected by the commutation C) from time to time between these experiments.

The curve runs parabolic fairly well as is expected from the foregoing reasoning. We obtained therefrom "the absolute single potential" of the normal calomel electrode as the potential at the minimum of the curve. The minimum of this parabola was determined as $+0.560 \pm 0.004$ volt at 20.1°C. by the method of the least square. The other series gave $+0.567 \pm 0.005$ volt at 21.0°C., giving $+0.563 \pm 0.004$ at 20.6°C. as the mean.

This value of "the absolute single potential" agrees very well with former ones given by the electrocapillary curve and the drop mercury electrode.

The authors wish to express thanks to Prof. J. Horiuti for his suggestions in the present work and valuable advices.

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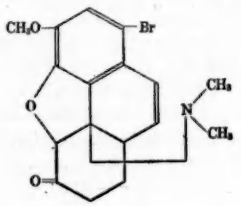
UNTERSUCHUNGEN ÜBER SINOMENIN. XLIII. MITTEILUNG.[1]

Von Kakuji GOTO und Hideo SHISHIDO.

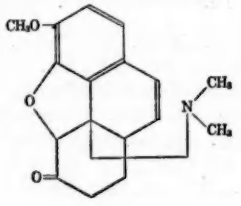
Eingegangen am 11. September, 1935. Ausgegeben am 28. Dezember, 1935.

I. Hofmannscher Abbau von Demethoxy-dihydro-sinomenin.

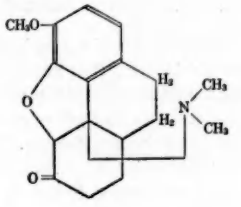
1-Brom-demethoxy-dihydro-sinomenein[2] und sein bromfreies Derivat[2] wurden in die zugehörige Des-N-methyl-basen umgewandelt und mit den entsprechenden Des-N-methyl-basen aus Dihydro-thebain racemisiert. Dabei wurden auch die Dihydro-des-N-methyl-basen (III) aus den beiden Quellen bereitet und racemisiert. Im Übergang von (+)- bzw. (−)-Dihydrokodeinon in die Des-N-methyl-base, hat der Drehungssinn nicht umgekehrt,[3] sondern das Drehungsvermögen stark abmindert. Ob dies von dem Oxyd-ring zwischen C_4 und C_5, oder von dem Drehungssinn von C_5[4] abhängt, ist zur Zeit nicht bekannt. Beim weiteren Abbau von Des-N-methyl-base, können wir noch nicht ein krystallisierender, N-freier Körper erhalten.[5]



I.



II.



III.

Des-N-methyl-1-brom-demethoxy-dihydro-sinomenein (I). 1 g. 1-Brom-demethoxy-dihydro-sinomeneinjodmethylat wurde mit 10 c.c. 2% Natronlauge 5 Min. lang gekocht. Das gebildete Öl wird aus Äthanol umkrystallisiert. Schmp. 130°. Ausbeute 0.3 g. (Gef.: C, 58.00; H, 5.65; Br, 20.19; N, 3.56. Ber. für $C_{19}H_{22}NO_3Br$ (392): C, 58.16; H, 5.61; Br, 20.41; N, 3.57%.) Spez. Drehung: 0.1 g. Subst. in 10 c.c. Methanol, 1 dm. Rohr, $\alpha = +0.07°$; $[\alpha]_D^{11} = +7.00°$. Diese Substanz bildet ein schön krystallisierendes Jodmethylat (Schmp. 278–279°), aber dessen Abbau noch nicht gelungen ist.

(1) XLII. Mitteilung, Dieses Bulletin, **10** (1935), 481

(2) *Ann.*, **489** (1931), 95.

(3) Thebenon-ringschluss lässt den Drehungssinn umkehren, Goto, *Ann.*, **485** (1931), 252.

(4) Im Morphin ist C_5 als linksdrehend angenommen, Emde, *Helvetica Chimica Acta*, **13** (1930), 1035.

(5) Vgl. M. Freund und E. Speyer, *Ber.*, **53** (1920), 2250.

Des-N-methyl-1-brom-dihydro-kodeinon (I). Darstellung wie oben. Schmp. 132°. (Gef.: N, 3.59. Ber. für $C_{19}H_{22}O_3NBr$ (392): N, 3.57%.) Spez. Drehung: 0.1 g. Subst. in 10 c.c. Methanol, 1 dm. Rohr, $\alpha = -0.08°$; $[\alpha]_D^{11} = -8.00°$.

***d, l*-Des-N-methyl-1-brom-dihydro-kodeinon.** Racemisiert wie gewöhnlich. Schmp. 148°; $\alpha = \pm 0$.

Des-N-methyl-demethoxy-dihydro-sinomenein (II). Diese Des-N-methyl-base wurde aus Demethoxy-dihydro-sinomenein[6] ganz wie ihr optischer Antipod aus Dihydro-kodeinon[7] dargestellt. Prismen, Schmp. 120°. (Gef.: N, 4.42. Ber. für $C_{19}H_{23}NO_3$ (313): N, 4.46%.) Spez. Drehung: 0.1 g. Subst. in 10 c.c. Methanol, 1 dm. Rohr, $\alpha = +0.04°$; $[\alpha]_D^{11} = +4.00°$.

Des-N-methyl-dihydro-kodeinon. Spez. Drehung: 0.1 g. Subst. in 10 c.c. Methanol, 1 dm. Rohr, $\alpha = -0.04$; $[\alpha]_D^{11} = -4.00°$.

***d, l*-Des-N-methyl-dihydro-kodeinon.** Bedingung der Racemisierung wie üblich. Schmp. 114–116°; $\alpha = \pm 0$.

Dihydro-des-N-methyl-demethoxy-dihydro-sinomenein (III). 0.7 g. Des-N-methyl-1-brom-demethoxy-dihydro-sinomenein wird in 100 c.c. 0.3% Salzsäure gelöst und mit 0.1 g. Palladiumchlorür und 0.2 g. palladiniertem $BaSO_4$ im Wasserstoff geschüttelt. Aufnahme des Wasserstoffes 90 c.c. in einer Stunde. Die befreite Base wird aus Äthanol-Äther umkrystallisiert. Schlanke Prismen, Schmp. 93–97°. Ausbeute 0.5 g. Keine Eisenchlorid- und Beilstein-reaktion. Löst sich in konz. Schwefelsäure farblos. (Gef.: C, 72.52; H, 8.15; N, 4.40. Ber. für $C_{19}H_{25}NO_3$ (315): C, 72.38; H, 7.94; N, 4.44%.) Spez. Drehung: 0.2000 g. Subst. in 10 c.c. Äthanol, 1 dm. Rohr, $\alpha = +1.00°$; $[\alpha]_D^{11} = +50.00°$.

Dihydro-des-N-methyl-dihydro-kodeinon (III). 0.8 g. Des-N-methyl-dihydro-kodeinon wird in 100 c.c. 2% Salzsäure gelöst und mit 0.2 g. $PdCl_2$ und 2 g. Kohle in Wasserstoffatmosphäre geschüttelt. Aufnahme des Wasserstoffes kommt zum Stillstand in 20 Min. (75 c.c.). Die Dihydro-des-N-base wird aus Äthanol-äther-gemisch umkrystallisiert. Schlanke Prismen, Schmp. 95–98°C. Eigenschaften wie in der (+)-Substanz. (Gef.: C, 72.66; H, 8.08; N, 4.53. Ber. für $C_{19}H_{25}NO_3$: C, 72.38; H, 7.94; N, 4.44%.) Spez. Drehung: 0.2000 g. Subst. in 10 c.c. Äthanol, 1 dm. Rohr, $\alpha = -1.01°$; $[\alpha]_D^{11} = -50.5°$.

***d, l*-Dihydro-des-N-methyl-dihydro-kodeinon.** Die racemische Substanz wurde dadurch bereitet dass man je 0.2 g. (+)- und (−)-Substanz, in Äthanol gelöst, vereinigte. Beim Einengen des Äthanols und Zusatz von Äther, krystallisierte die racemische Substanz in Rosetten. Ausbeute 0.3 g. Schmp. 113–116°C.; $\alpha = \pm 0$.

II. Katalytische Hydrierung von Thebain.

Bei der Bereitung von Dihydro-thebain nach Wieland und Kotake,[8] haben wir den Fall begegnet, in dem die Reducierung eine sehr lange Zeit in Anspruch nahm und die resultierende Substanz hauptsächlich aus Dihydro-kodeinon bestand. So haben wir einige Versuche über den Einfluss von Salzsäure-konzentration auf die katalytische Reduktion von Thebain gestellt,

(6) Dieses Bulletin, **5** (1930), 96.
(7) M. Freund und E. Speyer, *Ber.*, **53** (1920), 2250.
(8) *Ann.*, **444** (1925), 88.

obgleich es schon darüber eine ausführliche Arbeit von Schöpf[9] gibt. Sogar hat Cahn[10] durch katalytische Reducierung von roter Lösung von Thebain in rauchender Salzsäure Meta-thebainon in 81% Ausbeute erhalten. Unsere Resultate werden kurz in der folgenden Tabelle zusammengefasst.

	Konzentration von HCl	Thebain (g.)	Zeit-dauer	H_2 (c.c.)	Ausbeute
1	10 c.c. rauch. HCl 10 c.c. H_2O } ca. 5 N. (Die Lösung war nur fade gelb gefärbt.)	2	8 St.	135	Meta-thebainon (Schmp. 120–122°) 1.4 g. (75%)
2	20 c.c. ca. 2.5 N HCl	2	6 St.	150	Meta-thebainon (Schmp. 122–123°) 0.1 g. Dihydro-kodeinon (Schmp. 192–194°) 0.55 g. Dihydro-thebainon (Schmp. 153°) 0.15 g.
3	24 c.c. N HCl 5 c.c. H_2O	5	einige Tage	375	Dihydro-thebain 1.7 g. Dihydro-thebainon 0.2 g.

Aus dieser Tabelle ersieht man leicht dass eine stärkere Salzsäure (z.B. 2.5 N) das zuerst gebildete Dihydrothebain in der Kälte verseifen kann. Tatsächlich wurde Dihydro-thebain beim Stehenlassen über Nacht mit 2 N Salzsäure quantitativ ins Dihydro-kodeinon umgewandelt. Thebain selbst bleibt bei derselben Behandlung fast unangegriffen. Jedenfalls scheint die Reducierung von Thebain in konz. Salzsäure eine bequeme Darstellungsmethode von Meta-thebainon zu sein.

III. Isolierung von Demethoxy-dihydro-sinomenin über Bromhydrat.

In der XIX. Mitteilung[11] haben wir über die Mischkrystalle von Demethoxy-dihydro-sinomenin [(+)-Dihydro-thebainon] und Demethoxy-dihydro-sinomeninol [(+)-Dihydro-thebainol] berichtet, welche durch blosse Umkrystallisierung nicht voneinander getrennt werden können. Nun werde es gefunden dass die Trennung sehr leicht durch HBr oder HCl erzielt werden kann. Demethoxy-dihydro-sinomenin-bromhydrat krystallisiert sofort beim Lösen der Base in Bromwasserstoffsäure aus. Dicke Prismen, Schmp. 291° (Zers.). (Gef.: Br, 20.58. Ber. für $C_{18}H_{24}NO_3Br$ (382): Br, 20.94%). Das

(9) Schöpf, *Ann.*, **452** (1927), 244.
(10) R. S. Cahn, *J. Chem. Soc.*, **1933**, 1038.
(11) Dieses Bulletin, **5** (1930), 288.

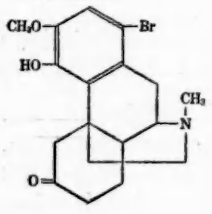
Chlorhydrat ist etwas löslicher. Schlanke Prismen, Schmp. 293° (Zers.). (Gef.: Cl, 10.60. Ber. für $C_{18}H_{24}NO_3Cl$ (337.5): Cl, 10.52%.)

(−)-Dihydro-thebainon bildet auch Bromhydrat und Chlorhydrat, die bei 291° bzw. 293° schmelzen. Diese Eigenschaft kann vorteilhaft benutzt werden, in der Darstellung von Dihydro-thebainon aus Thebain.[12]

(+)- und (−)-Dihydro-thebain, aus ihren Salzen befreit, schmelzen bei 152–153°[13] scharf und bilden das Oxim-chlorhydrat von Schmp. 317°.

IV. *d, l*-1-Brom-dihydro-thebainon.

C. Schöpf[14] gibt dem (−)-1-Brom-dihydro-thebainon (IV) den endgültigen Schmelzpunkt 167° an. Wir haben den Schmelzpunkt von 1-Brom-demethoxy-dihydro-sinomenin als 119° angegeben.[15] Da, aber, nach unseren Erfahrungen die entsprechenden (−)- und (+)-Derivate von Thebain und Sinomenin fast immer einen gleichen Schmp. zeigen, haben wir 1-Brom-demethoxy-dihydro-sinomenin vom Schmp. 167° darzustellen versucht. Und einmal haben wir die Substanz (5 g.) von Schmp. 167° bekommen, aber beim Umkrystallisieren aus Aceton kehrte der Schmp. zu 127° (mit Meniskusbildung bei 167°) zurück.[16] Dieses Verhalten erinnert uns an den zweierlei Schmp. von Sinomenin (159° bzw. 182°). Die Substanz von höherem Schmp. gewinnt man gelegentlich bei der schnellen Befreiung[17] der Base aus dem Chlorhydrat, z.B. Erhitzen auf 100°C. von dem Chlorhydrat mit $NaHCO_3$ in Wasser. Dieses Verfahren glückt, indessen, nicht immer.



IV.

Spez. Drehung von 1-Brom-dihydro-thebainon: 0.1500 g. Subst. in 10 c.c. Methanol + Chloroform, $\alpha = -1.16°$; $[\alpha]_D^{17} = -77.33°$.

Spez. Drehung von 1-Brom-demethoxy-dihydro-sinomenin[18]: 0.1500 g. Subst. in 10 c.c. Methanol + Chloroform, $\alpha = +1.18°$; $[\alpha]_D^{17} = +78.67°$.

Je 0.15 g. (−)- und (+)-1-Brom-dihydro-thebainon wurden in Methanol gelöst und vereinigt. Die racemische Substanz scheidet sich in sechsseitigen Tafeln aus. Schmp. 190–193°; $\alpha = \pm 0$.

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(12) Freund und Speyer, *Ber.*, **53** (1920), 2261.
(13) Skita's Angabe (Schmp. 137–138°), *Ber.*, **54** (1921), 1561, scheint zu niedrig zu sein.
(14) C. Schöpf und T. Pfeifer, *Ann.*, **483** (1930), 157.
(15) Dieses Bulletin, **5** (1930), 96.
(16) Das Oxim von 1-Brom-demethoxy-dihydro-sinomenin schmilzt bei 177–178° (Gef.: N, 6.77. Ber. für $C_{18}H_{23}O_3N_2Br$: N, 7.01%). Der Schmp. 263° [Dieses Bulletin, **5** (1930), 96] war leider derselbe vom Oximchlorhydrat.
(17) H. Kondo und E. Ochiai empfahlen die Befreiung mit konz. Ammoniak.
(18) Neu gemessen. Frühere Angabe war zu niedrig.

THE DIRECT INTRODUCTION OF DEUTERIUM INTO BENZENE BY HIGH FREQUENCY CURRENT.

By J. HORIUTI and T. KOYANO.

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It is known that deuterium can be directly introduced into benzene with heavy water at 200°C. in the presence of a metallic catalyst.[1] This method has been successfully applied by H. S. Taylor to the preparation of C_6D_6.[2]

We have found now that under the influence of the electromagnetic oscillator of high frequency deuterium can be introduced into benzene at room temperature, metallic catalyst being used.

In a vessel of 20 c.c. capacity with a flat bottom 0.25 c.c. of pure benzene was sealed together with 0.2 c.c. of 8% heavy water and 0.5 g. of platinum black prepared by reducing platinum chloride with formaldehyde. After the contents were subjected to the influence of high frequency wave for some time, the benzene was burnt and the formed water was analysed for the deuterium content.

In our first experiment the vessel was kept on a pole of a Tesla coil for ten hours and the benzene was found to have been shifted to 0.69% in the deuterium content. No temperature change was observed during the treatment. In the second experiment the vessel was kept between poles of the high frequency oscillator of 4 meter wave length. The vessel was cooled with water during the treatment. The deuterium content of the benzene was 0.41%.

Benzene was also treated similarly with ordinary water and it was found that physical constants were unaffected within the limit of the experimental errors: the density and the freezing point agreed with those of untreated benzene within 10^{-4} and 1/10°C. respectively.

It was found that even under the influence of the high frequency oscillator the exchange reaction did not take place without the catalyst. Further studies on the introduction of deuterium into organic compounds by this simple method will be carried on in our laboratory.

We wish to thank the Nippon Gakujutsu-Shinkôkai for a financial grant.

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1) J. Horiuti and M. Polanyi, *Nature*, **134** (1934), 377; *Trans. Faraday Soc.*, **30** (1934), 1164.

2) P. I. Bowman, W. S. Benedict, H. S. Taylor, *J. Am. Chem. Soc.*, **57** (1935), 960.

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CORRECTIONS

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Page	Line	
406	17*	*for* "secend" *read* "second"

Volume 10, 1935.

Page	Line	
5	4*	*for* "dada" *read* "data"
13	Table 7	*for* "Ethylene bromide" *read* "Ethyl bromide"
14	2	*for* "ethylene bromide" *read* "ethyl bromide"
17	12	*for* "Spärter" *read* "Später"
76	Formula (4)	insert a single bond between CH_2's
82	16*	*for* "into the faces" *read* "into the fæces"
245	Table 2	*for* "F. a. from filtrate 69.5 g., i.v. 322.3" "F. a. from 1st ppt. 25 g., i.v. 318.2" *read* "F. a. from ppt. 54 g., i.v. 314.5" "F. a. from filtrate (A_1) 36.5 g., i.v. 331.7"
291		replace the last two lines
314	14	*for* "difficulty" *read* "difficultly"
314	16	omit the comma after "if"
432	Figure	Ordinate: *for* "1/0000" *read* "1/10000"
439	16*	*for* "n_D^{20} 1.4934" *read* "$^{20}_{D}$ 1.5014"
504	2*	*for* "vs means" *read* "v's mean"

* From bottom.